

# Zero-, one-, two- and three-dimensional supramolecular architectures sustained by Se $\cdots$ O chalcogen bonding: A crystallographic survey

Edward R. T. Tiekink

Research Centre for Crystalline Materials, School of Science and Technology, 5 Jalan  
Universiti, Sunway University, Bandar Sunway, Selangor Darul Ehsan 47500, Malaysia

E-mail: [edwardt@sunway.edu.my](mailto:edwardt@sunway.edu.my)

ORCID ID: 0000-0003-1401-1520

## ABSTRACT

The Cambridge Structural Database was evaluated for crystals containing Se $\cdots$ O chalcogen bonding interactions. These secondary bonding interactions are found to operate independently of complementary intermolecular interactions in about 13% of the structures they can potentially form. This number rises significantly when more specific interactions are considered, e.g. Se $\cdots$ O(carbonyl) interactions occur in 50% of cases where they can potentially form. In about 55% of cases, the supramolecular assemblies sustained by Se $\cdots$ O(oxygen) interactions are one-dimensional architectures, with the next most prominent being zero-dimensional assemblies, at 30%.

Keywords: Supramolecular; chalcogen bonding; secondary bonding; selenium; oxygen

## Table of Contents

1. Introduction
2. Methodology
3. Zero-dimensional assemblies mediated by Se $\cdots$ O chalcogen bonding

- 3.1 Selenium(II) species
  - 3.1.1 Aggregates sustained by a single Se $\cdots$ O contact
  - 3.1.2 Aggregates sustained by two Se $\cdots$ O contacts
- 3.2 Selenium(IV) and selenium(VI) species
  - 3.2.1 Aggregates of selenium(IV) species sustained by two Se $\cdots$ O contacts
  - 3.2.2 Aggregates of selenium(IV) species sustained by more than two Se $\cdots$ O contacts
  - 3.2.3 Aggregates of selenium(VI) species sustained by Se $\cdots$ O contacts
- 4. One-dimensional assemblies mediated by Se $\cdots$ O chalcogen bonding
  - 4.1 Mono-nuclear selenium(II) species forming linear supramolecular chains
  - 4.2 Mono-nuclear selenium(II) species forming zig-zag supramolecular chains
  - 4.3 Mono-nuclear selenium(II) species forming helical and twisted supramolecular chains
  - 4.4 Multi-nuclear selenium(II) species forming supramolecular chains
    - 4.4.1 Bi-nuclear selenium(II) species forming linear chains
    - 4.4.2 Bi-nuclear selenium(II) species forming zig-zag chains
    - 4.4.3 Bi-nuclear selenium(II) species forming helical chains
    - 4.4.4 Multi-nuclear selenium(II) species forming supramolecular chains
  - 4.5 Multi-nuclear selenium(IV) species forming supramolecular chains
- 5 Two-dimensional assemblies mediated by Se $\cdots$ O chalcogen bonding
  - 5.1 Two-dimensional assemblies formed by selenium(II) compounds
  - 5.2 Two-dimensional assemblies formed by selenium(IV) compounds
- 6 Three-dimensional assemblies mediated by Se $\cdots$ O chalcogen bonding
- 7 Supramolecular assemblies of multi-component species mediated by Se $\cdots$ O chalcogen bonding
  - 7.1 Supramolecular assemblies in solvates of selenium compounds
  - 7.2 Supramolecular assemblies in selenium(II) co-crystals

7.3    Supramolecular assemblies in selenium(IV) co-crystals

8       Overview

9       Conclusions

Conflict of Interest

Acknowledgements

Appendix A: Supplementary Material

References

## 1. Introduction

Being present in the three domains of life, i.e. Archaea, Bacteria and Eukarya, selenocysteine has long been recognised as the 21<sup>st</sup> proteinogenic amino acid [1-3]. Natural biological functions of selenocysteine relate to redox moderation and anti-oxidant effects such as in the mammalian oxidoreductase system, thioredoxin reductase (TrxR), where it is present in the active site [4]. In connection with thyroid disease, selenocysteine is also present in the active sites of deiodinase enzymes which can activate or inactivate thyroid hormones [5]. The crucial role of selenium in natural biological functions implies a selenium-deficient diet causes disease and requires intervention [6]. Complimenting dietary supplements, synthetic selenium compounds also play a role/have potential as therapeutics [7-10]. The most prominent selenium drug is Ebselen<sup>TM</sup>, i.e. N-phenyl-1,2-benzisoselenazol-3(2H)-one, which is known to exhibit a variety of biological activities, partially owing to its ability to mimic the glutathione peroxidase enzyme, which regulates redox homeostasis and which protects cells from oxidative stress [7-10]. Other medicinal benefits of Ebselen<sup>TM</sup> include cytoprotective and neuroprotective properties, and potential therapeutic applications relate to anti-cancer, anti-bacterial and anti-inflammatory activities [7-10]. With this background, it is not surprising the biological mechanism(s) of Ebselen<sup>TM</sup> and related species have been investigated thoroughly [11,12]. These experimental and theoretical investigations often point to the importance of both inter- and intra-molecular Se...O interactions in crucial biological processes [11,12]. Stabilising Se...O interactions are now classified among chalcogen bonding interactions, a term possibly first employed in 1998 [15], whereby the Group XVI element functions as an electrophile [13,14]. It is stressed that the focus of the present review is upon the role of intermolecular Se...O contacts and upon the supramolecular aggregation patterns they sustain. In general terms, chalcogen interactions find very practical applications in a range of contexts beyond biology and medicine [16-18], such as in molecular/anion recognition [19-22], catalysts

[23,24] and materials science [25,26]. With this level of activity, it is not surprising there are several authoritative reviews of chalcogen bonding [27-30], including reviews of different physiochemical procedures for their detection in phases other than in crystals [31-33], the primary importance of X-ray crystallographic investigations notwithstanding.

The most convenient method for identifying chalcogen bonding in the solid-state relies upon crystal structure analysis with the earliest investigations of chalcogen bonding depending on the evaluation of crystal structures for contacts occurring at separations intermediate between the respective sums of the covalent and van der Waals radii for the participating atoms. In these present times where all manner of intermolecular contacts/supramolecular synthons are being “revealed”, it might be tempting to suggest chalcogen bonding, and related telluride and pnictogen interactions involving, respectively, Group XIV and XV elements acting as the electrophile, are a recent phenomenon. While obviously these interactions already exist in the crystals of the relevant compounds capable of forming such interactions and may not necessarily have been recognised or appreciated as being significant previously, it turns out the discussion of secondary bonding interactions actually goes back well over 50 years. Among the first bibliographic reviews of the topic are those by H.A. Bent [34], Noble Laureate O. Hassel [35] and N.W. Alcock [36], with these being followed up by a number of general overviews of the topic [37-40]. It is likely the first time the term secondary bonding was used in the context of these donor-acceptor interactions appeared in the title of a research paper was in a Conference Abstract published in 1975 [41] and then in a follow-up Journal article in 1977 [42]. The use of secondary bonding as a design element in crystal engineering endeavours was suggested as early as 1999 [43].

An initially disconcerting feature of many secondary bonding interactions, including halogen bonding [44], which also comes under the appellation secondary bonding [36], was that the interaction often occurred between two electron-rich species, i.e. a low oxidation state

main group element, implying a lone-pair or even lone-pairs of electrons, and donors also having at least one lone-pair of electrons. Through the concept of a  $\sigma$ -hole, theory now aids the understanding of this apparent violation of basic electrostatic arguments. Conventionally the bonding in chalcogen bonds was described in terms of charge transfer from a lone-pair of electrons of the donor atom (D) to an anti-bonding orbital of the bond involving the chalcogen atom (A–X), i.e.  $(D)n^2 \rightarrow \sigma^*(A-X)$ , but the problem remains in that two electron-rich species are brought into close contact. The  $\sigma$ -hole concept, widely employed to explain the bonding in such circumstances [45,46], relates to the anisotropic distribution of charge about the bonded chalcogen atom. With reference to the bonding axis of a A–X bond, there is an equatorial band of electron density about the A atom, i.e. perpendicular to the A–X bond, and a significant electron-deficient region at the extension of the bonding axis, the  $\sigma$ -hole (or polar cap). It is the latter that can form stabilising interactions with nucleophilic species. The success and general applicability of this approach in rationalising the formation of chalcogen bonds as well as tetrel, pnictogen and halogen bonds [47] notwithstanding, recent studies point to the importance of orbital delocalisation as being relevant [48]. Having a model for bonding, the question then arises as to what are the energies of stabilisation are provided by chalcogen and related interactions. Naturally, the calculated energies will be highly dependent on the nature of the bonds about the interacting atoms, steric profiles of the interacting residues and whether a chalcogen or other intermolecular interaction is operating independently of supporting or competing intermolecular interactions not to mention the level of theory/basis sets employed in the performing of the calculations. Nevertheless, there appears a consensus from calculations [49-53] that the energies of stabilisation afforded by secondary bonding interactions are comparable and often exceed those provided by conventional hydrogen bonding interactions [54] and which, in turn, are comparable to the energies associated with

other supramolecular synthons involving heavy elements such as  $\pi(\text{chelate ring})\cdots\pi(\text{chelate})$  interactions [55].

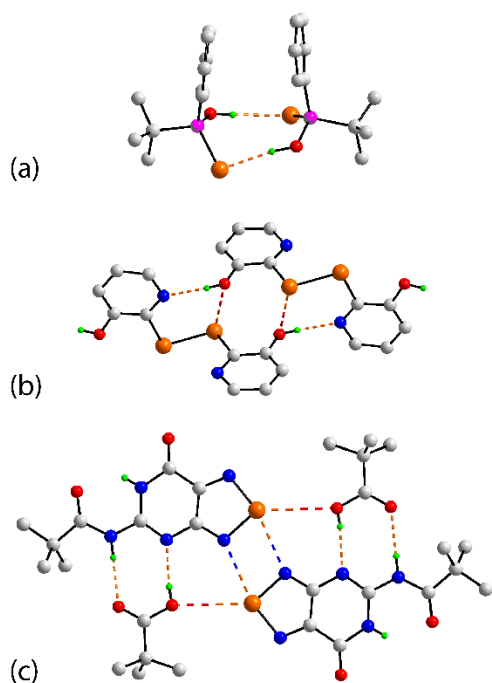
It was in the context of a long-held interest in secondary bonding interactions and the supramolecular architectures they sustain [56-64] and in the aforementioned biological relevance of  $\text{Se}\cdots\text{O}$  chalcogen bonding interactions that the present survey of  $\text{Se}\cdots\text{O}$  interactions operating in crystals was undertaken. This review of the crystallographic literature serves to highlight the diverse nature of selenium atom environments, geometries, oxidation states and numbers and types of  $\text{Se}\cdots\text{O}$  secondary bonding interactions formed by selenium and the wide variety of supramolecular architectures these chalcogen bonding interactions sustain.

## 2 Methodology

The Cambridge Structural Database (CSD; version 5.41) [65] was searched employing ConQuest (version 2.0.4) [66] for  $\text{Se}\cdots\text{O}$  contacts present in crystals based on the distance criterion that the separation between the selenium and oxygen atoms had to be equal to or less than the sum of the van der Waals radii, i.e. assumed in the CSD as 3.42 Å [65]. Other general criteria were applied in order to keep the number of retrieved structures to a reasonable number and to ensure reliability in the data, namely structures with errors, were charged, polymeric and contained transition metal elements were omitted along with those with  $R > 0.075$ . In all 274 structures were retrieved. These were then evaluated manually to ensure that the  $\text{Se}\cdots\text{O}$  interaction was operating in isolation of other obvious supramolecular synthons employing PLATON [67], Mercury [68] and DIAMOND [69].

Three classes of compounds were rejected from further analysis. Firstly, several structures that registered as the hit was in fact a false positive as the putative  $\text{Se}\cdots\text{O}(\text{hydroxyl})$  interaction (3.30 Å) was embedded within a hydroxyl- $\text{O}-\text{H}\cdots\text{Se}$  hydrogen bond. This is illustrated in Fig. 1a for (-)-*t*-butylphenylphosphinoselenoic acid [70], where hydroxyl- $\text{O}-$

H $\cdots$ Se hydrogen bonding occurs between the two independent molecules comprising the asymmetric unit in the crystal. The second scenario leading to the omission of structures also involved hydrogen bonding. Thus, in bi-nuclear 2,2'-(diselane-1,2-diyl)bis(pyridin-3-ol) [71], two centrosymmetrically related molecules are connected into a dimeric aggregate via hydroxyl-O–H $\cdots$ N(pyridyl) hydrogen bonds as shown in Fig. 1b. Contributing to the stability of this aggregate are Se $\cdots$ O(hydroxyl) contacts (3.36 Å) which, obviously, are not operating independently and so examples such as this were omitted from the survey. The third class of omitted compounds featured complementary secondary bonding interactions. An example of this is shown in Fig. 1c where some of the supramolecular association operating in the 1:1 co-crystal formed between co-formers 2,2-dimethyl-N-(7-oxo-6,7-dihydro[1,2,5]selenadiazolo[3,4-d]pyrimidin-5-yl)propanamide and 2,2-dimethylpropanoic acid [72] are highlighted. While Se $\cdots$ O interactions (3.27 Å) are noted, these occur within a tetra-molecule assembly sustained by Se $\cdots$ N secondary bonding interactions (2.83 Å) and eight-membered { $\cdots$ HOCO $\cdots$ NCNH} synthons.





**Fig. 1.** Examples of excluded structures from the present survey owing to (a) the Se $\cdots$ O contact being embedded within a hydroxyl-O–H $\cdots$ Se hydrogen bond, (b) the Se $\cdots$ O contact occurring within an assembly also mediated by hydroxyl-O–H $\cdots$ N(pyridyl) hydrogen bonds and (c) the Se $\cdots$ O contacts occurring within a tetra-molecule aggregate already sustained by a combination of Se $\cdots$ N secondary bonding interactions and hydrogen bonding. Hydrogen bonds are shown as orange dashed lines, Se $\cdots$ O contacts as orange-red dashed lines and Se $\cdots$ N contacts as orange-blue dashed lines. In this and subsequent diagrams, only acidic-H atoms are shown. Colour code: selenium (orange), phosphorus (pink), oxygen (red), nitrogen (blue), carbon (grey) and hydrogen (green).

After manual screening, there remained 224 examples of supramolecular aggregation featuring Se $\cdots$ O secondary bonding interactions. All of these are illustrated in Appendix A along with detail of the full composition of the crystal, citation details, selected distances and angles, and comments on supramolecular aggregation along with image(s). The structures are generally arranged in terms of the supramolecular aggregation patterns sustained by the Se $\cdots$ O secondary bonding interactions operating in the crystals, i.e. zero-, one-, two- and three-dimensional. For completeness, Se $\cdots$ O interactions occurring in solvates and co-crystals are also included. Within each of these categories, discussion of selenium(II) atoms participating in Se $\cdots$ O interactions precedes those involving selenium(IV) centres and, when known, selenium(VI) examples. Within in each oxidation state, mono-nuclear species are covered before bi-nuclear species, etc. and within each of these categories, aggregates sustained by one interaction are illustrated before those sustained by two interactions, etc. Generally, the examples are included in order of increasing Se $\cdots$ O distances. The exception to the last guideline occurs when there are significant numbers of closely related compounds. Comments on hydrogen bonding, when present in the crystal, are also included in Appendix A rather than

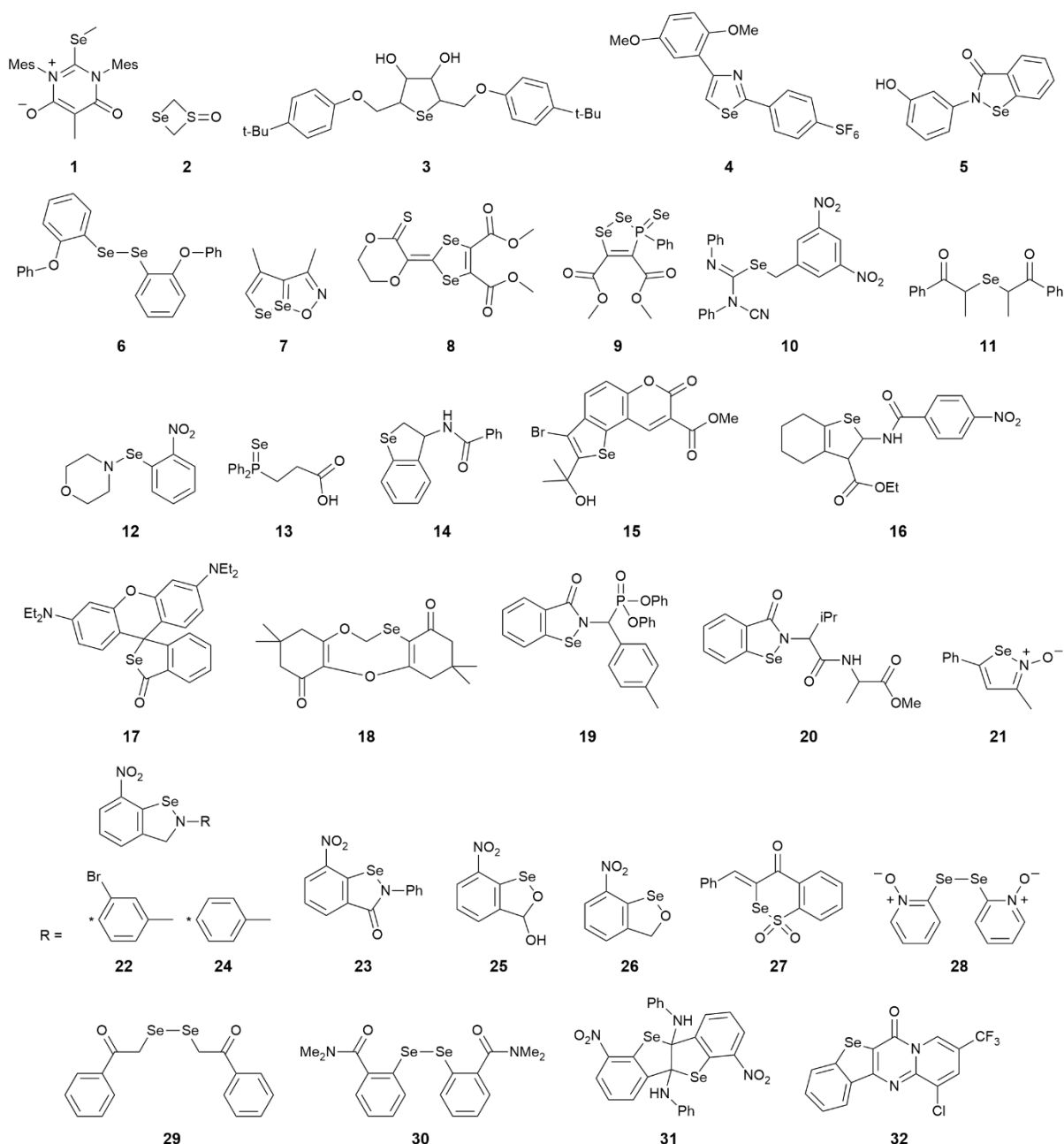
in the main text unless pertinent to the discussion of the identified  $\text{Se}\cdots\text{O}$  contacts. Finally, while the focus herein is upon intermolecular  $\text{Se}\cdots\text{O}$  contacts, hypervalent intramolecular  $\text{Se}\cdots\text{O}$ , and more rarely  $\text{Se}\cdots\text{F}$  and  $\text{Se}\cdots\text{S}$  contacts, are noted in a number of the structures included in this survey. In cases where these occur, details are also included in Appendix A.

### **3 Zero-dimensional assemblies mediated by $\text{Se}\cdots\text{O}$ chalcogen bonding**

In 55 structures zero-dimensional assemblies are formed mediated by  $\text{Se}\cdots\text{O}$  chalcogen bonding interactions. These can be connected by one  $\text{Se}\cdots\text{O}$  contact, usually two  $\text{Se}\cdots\text{O}$  contacts but aggregates sustained by up to 10  $\text{Se}\cdots\text{O}$  contacts are known. Selenium(II), (IV) and (VI) species are all shown to form zero-dimensional aggregates.

#### **3.1 Selenium(II) species**

There are a total of 32 selenium(II) species, **1–32** [11,73-96,98-101], forming  $\text{Se}\cdots\text{O}$  contacts leading to zero-dimensional aggregates. The chemical diagrams for the interacting species in these structures are shown in Fig. 2.

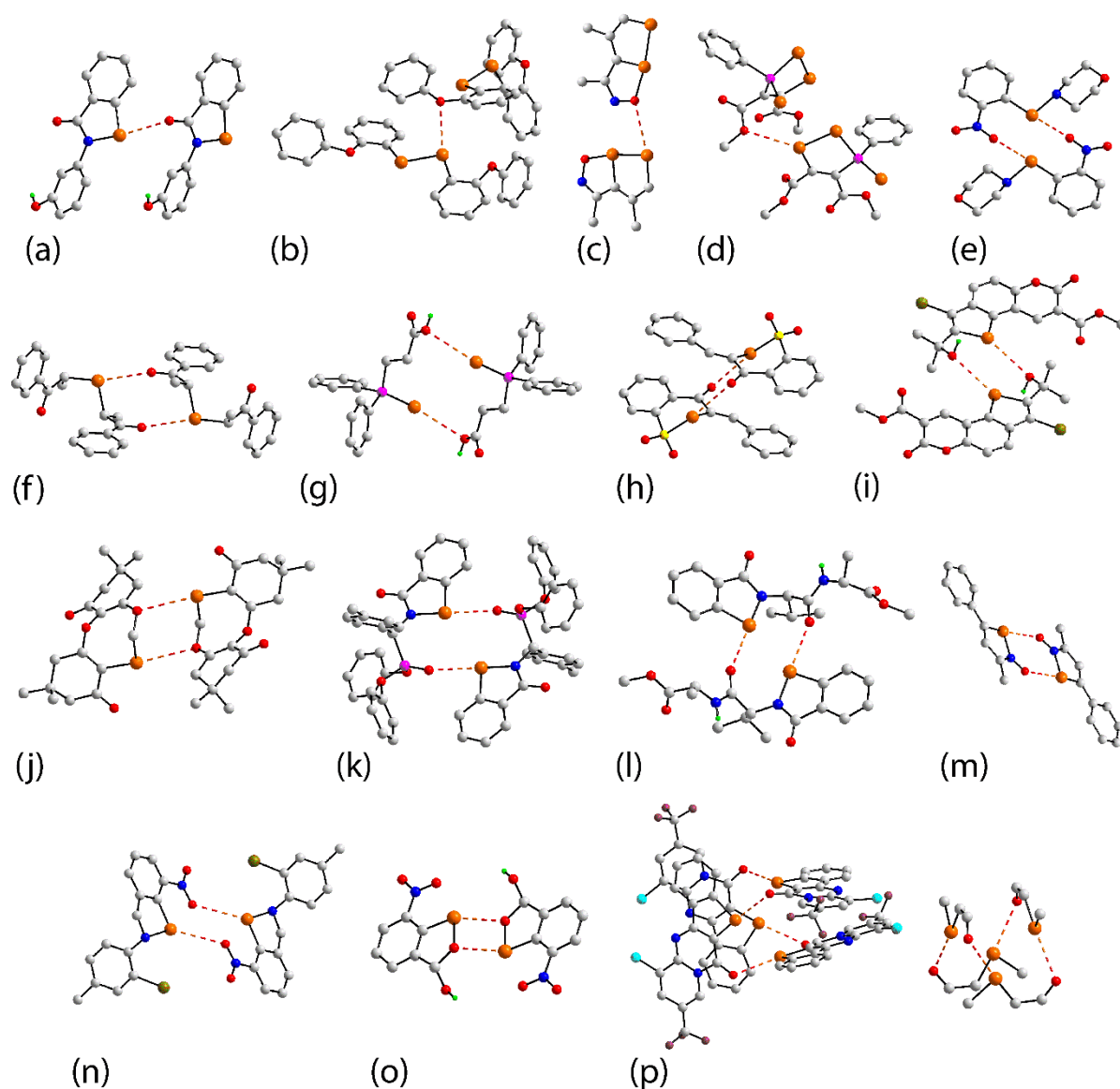


**Fig. 2.** Chemical diagrams for the interacting species, 1–32, in selenium(II) compounds featuring Se...O contacts leading to zero-dimensional aggregates. The point of attachment at the nitrogen atom in 22 is indicated by an asterisk.

### 3.1.1 Aggregates sustained by a single Se...O contact

The common feature of mono-selenium(II) molecules 1–5 [11,73-76] is that dimeric aggregates are sustained by a single Se...O chalcogen bonding interaction; in each of 2–5, the

selenium atom is incorporated within a ring. For **2** [74], **4** [76] and **5** [11], Fig. 3a, the contact forms between the two independent molecules comprising the crystallographic asymmetric unit. In **1** [73], there are four independent molecules and two pairs are connected by a single  $\text{Se}\cdots\text{O}(\text{carbonyl})$  interaction. In **3** [75], there are eight independent selenium(II)-containing molecules and four DMSO molecules in the asymmetric unit. In this instance, only one pair of selenium(II)-containing molecules is connected by a single  $\text{Se}\cdots\text{O}(\text{hydroxyl})$  contact. This is a relatively rare case as, usually, in cases where multiple molecules comprise the crystallographic asymmetric unit, all participate in the formation of  $\text{Se}\cdots\text{O}$  contacts (*vide infra*). In diselenide **6** [77], a  $\text{Se}\cdots\text{O}(\text{ether})$  interaction is featured between the two independent molecules of the asymmetric unit, Fig. 3b. Compound **7** [78] features both selenium(II) and selenium(IV) centres connected within a ring with the selenium(II) atom of one of these connecting to an oxygen atom of the second independent molecule via a  $\text{Se}\cdots\text{O}(\text{N-oxo})$  contact as shown in Fig. 3c. In **8** [79], with four independent molecules in the asymmetric unit, two pairs of molecules are connected by a single  $\text{Se}\cdots\text{O}(\text{methoxy})$  contact. A similar situation pertains in tri-nuclear **9** [80], where a single  $\text{Se}\cdots\text{O}(\text{methoxy})$  contact links the two independent molecules, Fig. 3d. The molecule of **9** is notable in that in addition to two ring selenium atoms, a phosphorus-bound selenide selenium(II) atom is present but, it is one of the ring selenium atoms that engages in the  $\text{Se}\cdots\text{O}(\text{methoxy})$  interaction. Despite the presence of multiple selenium atoms in **6-9**, only one of the possible selenium atoms in each is engaged in a  $\text{Se}\cdots\text{O}$  contact.



**Fig. 3.** Representative examples of supramolecular association in selenium(II) compounds leading to zero-dimensional aggregation patterns based on  $\text{Se}\cdots\text{O}$  chalcogen bonding interactions: (a) **5** [11;  $\text{Se}\cdots\text{O} = 2.96 \text{ \AA}$ ], (b) **6** [77;  $3.25 \text{ \AA}$ ], (c) **7** [78;  $3.41 \text{ \AA}$ ], (d) **9** [80;  $3.31 \text{ \AA}$ ], (e) **12** [83;  $3.34 \text{ \AA}$ ], (f) **11** [82;  $3.27 \text{ \AA}$ ], (g) **13** [84;  $3.36 \text{ \AA}$ ], (h) **27** [96;  $3.14 \text{ \AA}$ ], (i) **15** [86;  $3.27 \text{ \AA}$ ], (j) **18** [89;  $3.37 \text{ \AA}$ ], (k) **19** [90;  $2.80 \text{ \AA}$ ], (l) **20** [91;  $2.85 \text{ \AA}$ ], (m) **21** [92;  $2.93 \text{ \AA}$ ], (n) **22** [93;  $3.24 \text{ \AA}$ ], (o) **25** [95;  $2.91 \text{ \AA}$ ] and (p) **32** [101;  $2.98 \text{ \AA}$ ] (including simplified view). Additional colour codes: bromide (olive-green), chloride (cyan), yellow (sulphur), fluoride (plum).

### 3.1.2 Aggregates sustained by two Se $\cdots$ O contacts

The overwhelming majority of mono-nuclear selenium(II) molecules in this category adopt a two-molecule motif sustained by two Se $\cdots$ O contacts. This motif is found in the crystals of **10**–**27** [81-96]. Molecules **10**–**12** feature acyclic, two-coordinated selenium, **13** is a selenide and those of **14**–**27** are also two-coordinated but with the selenium atom incorporated within a ring. In **10** [81] and **20** [91] the Se $\cdots$ O interactions occur between the two independent molecules comprising the asymmetric unit whereas in the remaining examples, they occur between centrosymmetrically related molecules. The selenium atoms in **10** [81] and **12** [83], Fig. 3e, associate with nitro-oxygen atoms, in **11** [82] with carbonyl-oxygen, Fig. 3f, and in **13** [84], Fig. 3g, with hydroxyl-oxygen, the selenium donor being a phosphorous-bound selenide atom. While attention is directed towards intermolecular Se $\cdots$ O interactions in the present survey, it is worth highlighting here that several of these species discussed herein also feature close intramolecular Se $\cdots$ O contacts. This feature first occurs in **12** where, owing to the close proximity of a pendant nitro substituent, an intramolecular Se $\cdots$ O(nitro) contact of 2.58 Å occurs which is significantly shorter than the intermolecular Se $\cdots$ O(nitro) separation of 3.34 Å. While details of these intramolecular Se $\cdots$ O contacts, and rare examples of intramolecular Se $\cdots$ F and Se $\cdots$ O contacts, are not discussed herein comments on these are included in Appendix A.

The ring-selenium atoms are generally incorporated within five-membered rings but form part of a six membered ring in **27** [96] and part of an eight-membered ring in **18** [89]. The molecules in **14** [85], **16** [87] and **27** [96], the latter having potential sulfoxide-oxygen atoms capable of forming Se $\cdots$ O contacts, Fig. 3h, associate via Se $\cdots$ O(carbonyl) contacts. In the crystals of **15** [86], Se $\cdots$ O(hydroxyl) contacts are formed despite the presence of bromide atoms, Fig. 3i, and in each of **17** [88] and **18** [89], Fig. 3j, Se $\cdots$ O(ether) contacts are formed despite the presence of potential carbonyl-oxygen donors. Phosphorus-bound oxide atoms provide the oxygen atoms to form the dimeric aggregate in **19** [90], Fig. 3k, amide-O in **20**

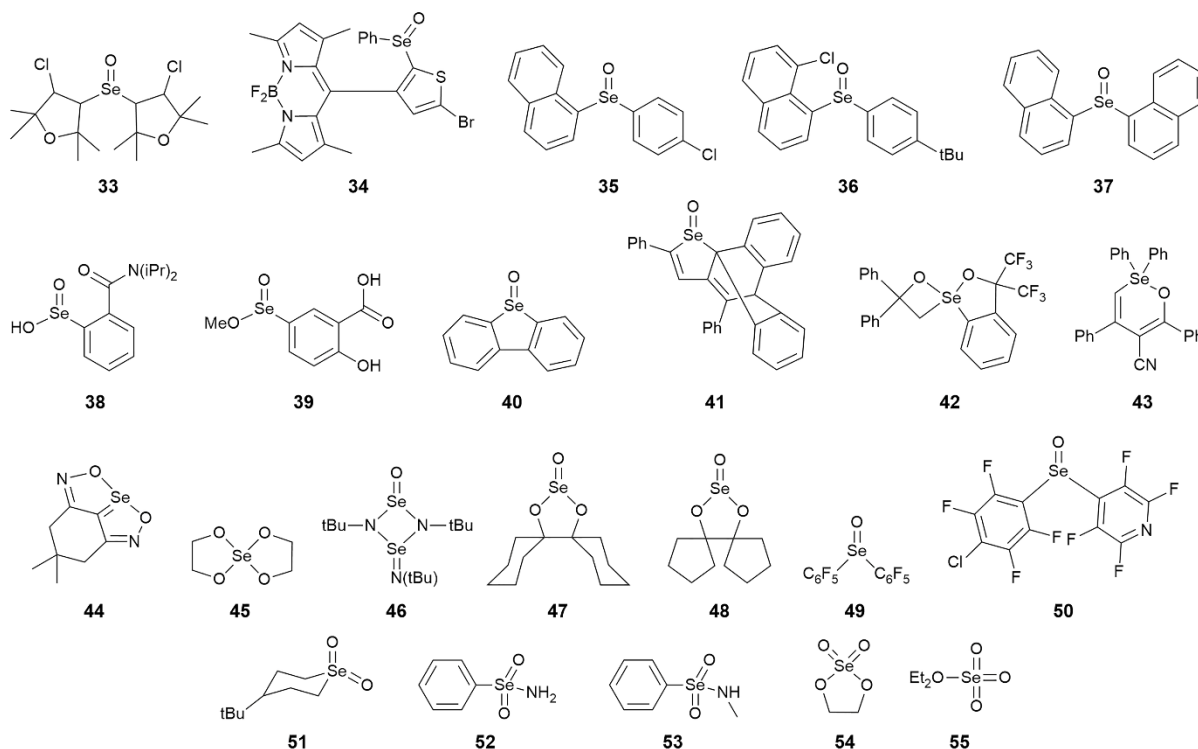
[91], Fig. 3l, and N-oxide in **21** [92], Fig. 3m. The dimeric aggregates formed in **22** [93], Fig. 3n, **23** [94] and **24** [93] are sustained by  $\text{Se}\cdots\text{O}(\text{nitro})$  interactions despite the presence of potential competitive interactions with bromide (**22**) and carbonyl-O (**23**). The two remaining molecules in this section feature adjacent selenium and oxygen atoms in the five-membered ring and each of these, i.e. **25** [95] and **26** [95], assemble about a centre of inversion to form a supramolecular four-membered  $\{\cdots\text{Se}-\text{O}\}_2$  synthon. In **25**, Fig. 3o, there are nitro- and hydroxyl-oxygen atoms also capable of forming  $\text{Se}\cdots\text{O}$  interactions but, do not. A related  $\{\cdots\text{Se}-\text{N}\}_2$  synthon was observed in Fig. 1c and has been discussed in terms of being a reliable synthon in the supramolecular chemistry of selenium-nitrogen materials [97]. The foregoing highlights the fact that a myriad of oxygen atoms can participate in  $\text{Se}\cdots\text{O}$  interactions and no definitive preference for one type oxygen atom over another is obvious.

There are four examples of bi-nuclear selenium(II) species forming centrosymmetric aggregates. In diselenide **28** [98],  $\text{Se}\cdots\text{O}(\text{N-oxide})$  interactions sustain the dimer while  $\text{Se}\cdots\text{O}(\text{carbonyl})$  contacts are found in each of **29** [99] and **30** [100]. In **31** [93], one of the ring-selenium atoms of the bi-nuclear molecule associates with a nitro-oxygen atom, similar to that seen in Fig. 3n. An extraordinary mode of association via  $\text{Se}\cdots\text{O}(\text{carbonyl})$  contacts is found in **32** [101]. Here, a four-molecule aggregate is formed about a four-fold rotatory inversion axis ( $\bar{4}$ ) as shown in the images of Fig. 3p.

### 3.2 Selenium(IV) and selenium(VI) species

Less common but, nevertheless well represented in this survey are selenium(IV) compounds, which differ by having a single lone-pair of electrons as opposed to two for selenium(II) species. Even less frequently observed herein are selenium(VI) species, devoid of stereochemically-active lone-pairs on the selenium centre. The interactions selenium(VI) species form with oxygen reflect more conventional Lewis acid-Lewis base interactions. There

are 18 selenium(IV) species, **33–50** [100,102-115], and five selenium(VI) species, **51–55** [116-119], forming  $\text{Se}\cdots\text{O}$  contacts leading to zero-dimensional aggregates, with the chemical diagrams for the interacting species in these shown in Fig. 4.



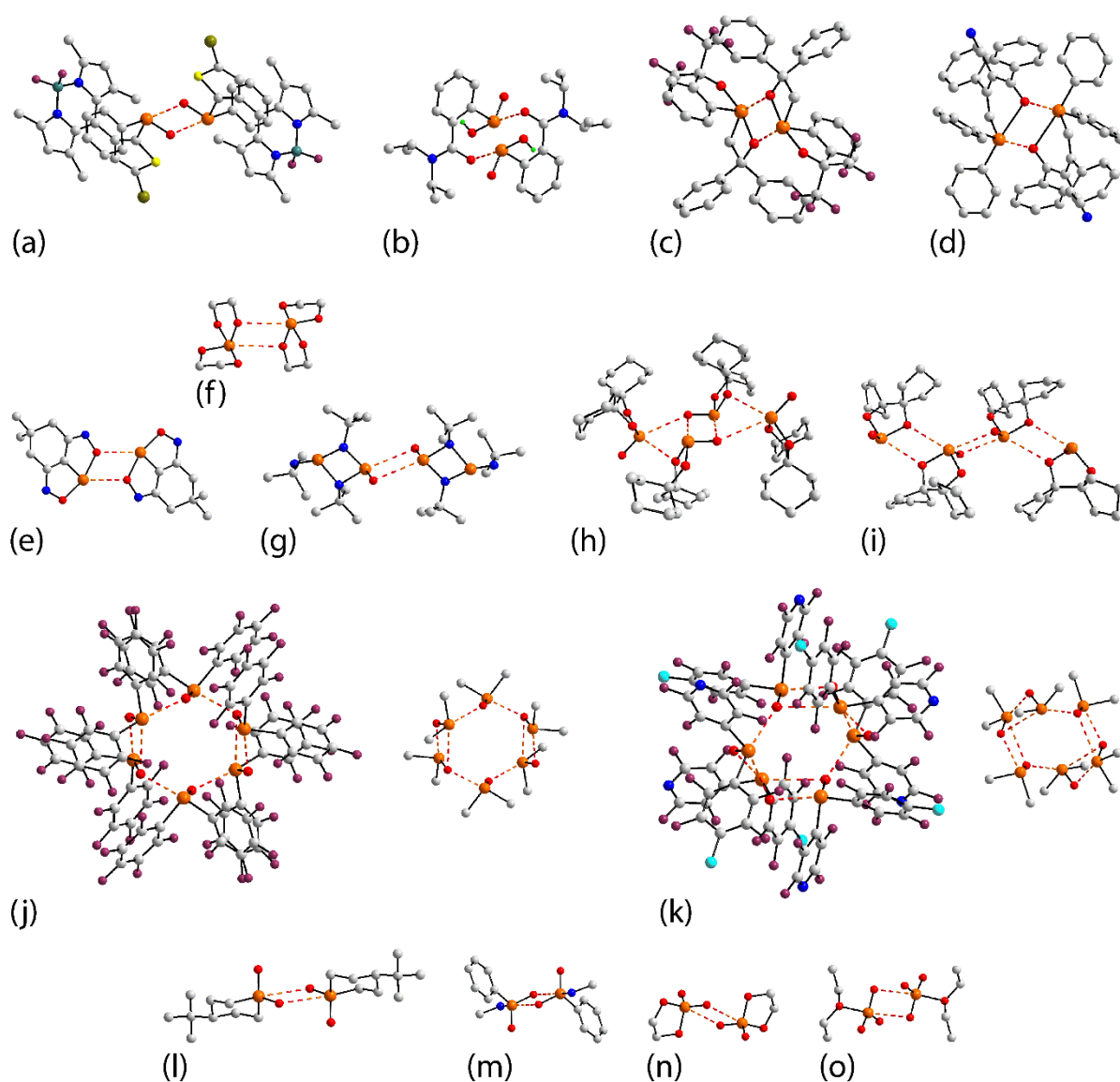
**Fig. 4.** Chemical diagrams for the interacting species, **33–55**, in selenium(IV) and selenium(VI) compounds featuring  $\text{Se}\cdots\text{O}$  contacts leading to zero-dimensional aggregates.

### 3.2.1 Aggregates of selenium(IV) species sustained by two $\text{Se}\cdots\text{O}$ contacts

The majority of the selenium(IV) compounds form centrosymmetric dimers, indeed 14 of the 18 crystals feature this motif, and each of these is constructed about a four-membered  $\{\cdots\text{Se}-\text{O}\}_2$  synthon. Compounds **33** [102], **34** [103], **35–37** [104] conform to the general formula  $\text{R(R')Se=O}$ . The dimeric aggregate for **34**, being representative for this series, is shown in Fig. 5a, is sustained by  $\text{Se}\cdots\text{O}(\text{oxide})$  interactions and is notable for the presence of potentially competitive but, non-interacting sulphur, fluoride and bromide donors. Two structures conform to the formula  $\text{R(R'O)Se=O}$ . In **38** [100], with  $\text{R}' = \text{H}$ , the interaction



sustaining the dimer is  $\text{Se}\cdots\text{O}(\text{carbonyl})$ , Fig. 5b, while the  $\text{Se}\cdots\text{O}(\text{oxide})$  interactions persist in **39** [105],  $\text{R}' = \text{Me}$ . Similar  $\text{Se}\cdots\text{O}(\text{oxide})$  interactions sustain dimers in instances when the selenium is incorporated in a five-membered ring as in the crystals of **40** [106] and **41** [107]. The first non-selenium oxide molecule in this section is **42** [108], Fig. 5c, where the selenium atom is C,O-chelated by two distinct ligands leading to four- and five-membered rings; the dimer is stabilised by  $\text{Se}\cdots\text{O}(\text{alkoxide})$  contacts. A similar contact occurs in the triorganoselenium species **43** [109], Fig. 5d, where the selenium atom is incorporated within a six-membered ring. The molecules in **44** [110], Fig. 5e, are connected by  $\text{Se}\cdots\text{O}(\text{N-oxo})$  interactions and those in **45** [111], Fig. 5f, and bi-nuclear **46** [112], Fig. 5g, by  $\text{Se}\cdots\text{O}(\text{alkoxide})$  and  $\text{Se}\cdots\text{O}(\text{oxide})$  interactions, respectively. The structure of **44** is the earliest reported crystal structure included in the present survey, being described in 1972. It is also noted here that the authors of this paper discussed the supramolecular association mediated by  $\text{Se}\cdots\text{O}$  secondary bonding in their description of the molecular packing in this crystal. Higher nuclearity aggregates are noted in the remaining selenium(IV) structures to be described in this section.



**Fig. 5.** Representative examples of supramolecular association in selenium(IV) and selenium(VI) compounds leading to zero-dimensional aggregation patterns based on  $\text{Se}\cdots\text{O}$  chalcogen bonding interactions: (a) **34** [103;  $\text{Se}\cdots\text{O} = 2.92 \text{ \AA}$ ], (b) **38** [100;  $2.85 \text{ \AA}$ ], (c) **42** [108;  $3.22 \text{ \AA}$ ], (d) **43** [109;  $3.00 \text{ \AA}$ ], (e) **44** [110;  $3.20 \text{ \AA}$ ], (f) **45** [111;  $3.29 \text{ \AA}$ ], (g) **46** [112;  $3.19 \text{ \AA}$ ], (h) **47** [113;  $2.81\text{--}3.24$ ], (i) **48** [113;  $2.96\text{--}3.20 \text{ \AA}$ ], (j) **49** [114;  $2.60\text{--}3.20 \text{ \AA}$ ], (k) **50** [115;  $2.66\text{--}3.33 \text{ \AA}$ ], (l) **51** [116;  $3.35 \text{ \AA}$ ], (m) **53** [117;  $3.23 \text{ \AA}$ ], (n) **54** [118;  $3.17 \text{ \AA}$ ] and (o) **55** [119;  $3.11 \text{ \AA}$ ]; the cores in hexameric **49** and **50** are also included.

### 3.2.2 Aggregates of selenium(IV) species sustained by more than two $\text{Se}\cdots\text{O}$ contacts

Each of **47** and **48** [113] assemble into tetrameric aggregates in the solid-state. In the crystal of **47**, there are two independent molecules in the asymmetric unit. One of these assembles about a centre of inversion by the familiar four-membered  $\{\cdots\text{Se}-\text{O}\}_2$  synthon. Attached to either side of this aggregate are two of the second independent molecules whereby each selenium of each of the terminal molecules effectively bridges the oxo atom, already engaged in a  $\text{Se}\cdots\text{O}$  contact implying this atom is bifurcated, and an alkoxide-oxygen atom of the O,O-chelating ligand, Fig. 5h. The tetrameric aggregate in **48**, Fig. 5i, has the same centrosymmetric  $\{\text{Se}\cdots\text{O}\}_2$  core but, the terminal connections are also of the type  $\{\text{Se}\cdots\text{O}\}_2$ , also formed by the second independent molecules. This compound is of particular interest as the asymmetric unit comprises four independent molecules. Two engage as shown in Fig. 5i, while the other two engage to form a supramolecular chain as discussed below, see **175** [113]. The last two selenium(IV) aggregates to be described are hexamers.

In the crystal of **49** [114], three independent molecules comprise the asymmetric unit. A hexagon of selenium atoms, with a pronounced chair conformation, is formed about a centre of inversion, with the connections between them being of the type  $\text{Se}\cdots\text{O}(\text{oxide})$ , Fig. 5j. In this scheme, two of the independent molecules associate via the four-membered  $\{\cdots\text{Se}-\text{O}\}_2$  synthon with two of these bridged by two of the third independent molecules. Thus, two of the selenium atom forms two  $\text{Se}\cdots\text{O}(\text{oxide})$  contacts and four make a single  $\text{Se}\cdots\text{O}(\text{oxide})$  contact. In terms of the oxide donors, two form two  $\text{Se}\cdots\text{O}(\text{oxide})$  contacts and the remaining four oxide-oxygen atoms participate in a single contact, indicating the hexamer is sustained by eight  $\text{Se}\cdots\text{O}(\text{oxide})$  interactions in all. A related situation pertains for the hexamer formed in the crystal of **50** [115], Fig. 5k. The core and asymmetry in the hexamer comprising **50** is as described for **49**. However, in the case of **50**, there are two independent and linked  $\{\cdots\text{Se}-\text{O}\}_2$  synthons which are bridged over the centre of inversion via a pair of  $\text{Se}\cdots\text{O}(\text{oxide})$  interactions.

So, four of the selenium atoms form two  $\text{Se}\cdots\text{O}(\text{oxide})$  contacts and two make a single  $\text{Se}\cdots\text{O}(\text{oxide})$  contact, leading to a total of 10  $\text{Se}\cdots\text{O}(\text{oxide})$  contacts sustaining the hexamer.

### 3.2.3 Aggregates of selenium(VI) species sustained by $\text{Se}\cdots\text{O}$ contacts

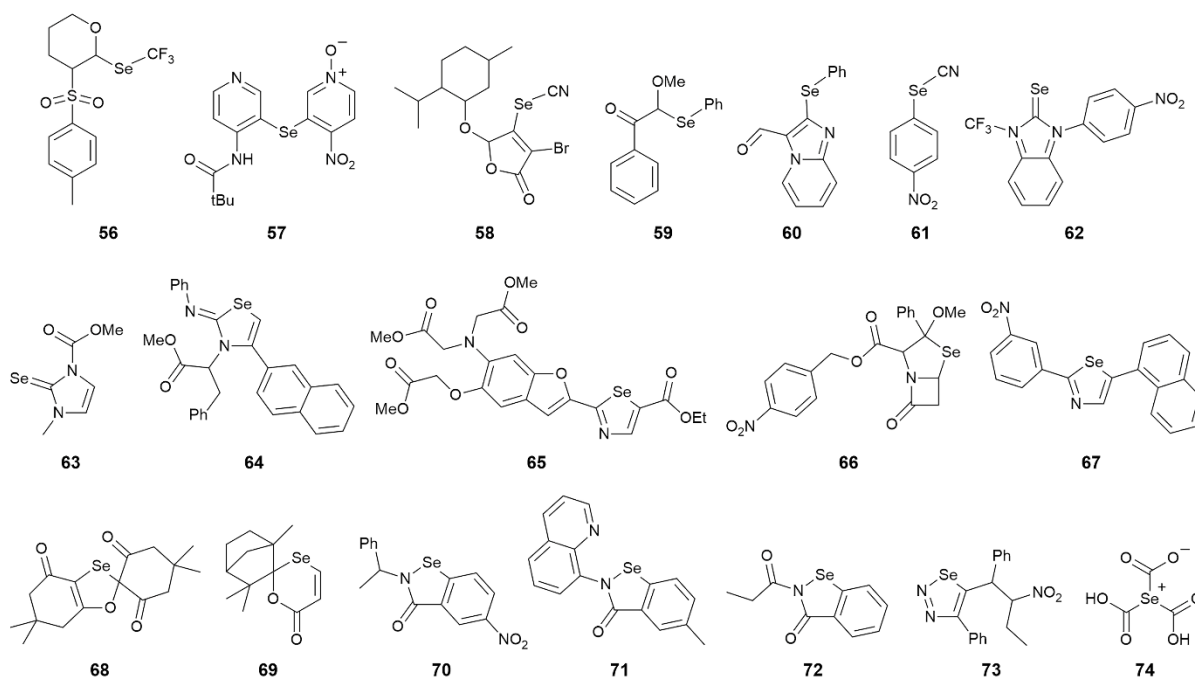
There are five selenium(VI) species featuring  $\text{Se}\cdots\text{O}$  interactions, each leading to a centrosymmetric, dimeric aggregate. Compounds **51** [116], **52** [117], **53** [117] and **54** [118] feature  $\text{Se}(=\text{O})_2$  entities, while that of **55** [119] is an adduct of  $\text{Se}(=\text{O})_3$ . A  $\{\cdots\text{Se}-\text{O}\}_2$  core is found in each of the five dimers. In diorgano **51**, the selenium atom is incorporated within a six-membered ring, Fig. 5l. Two species feature  $\text{CNO}_2$  coordination geometries, i.e. **52** and **53**, Fig. 5m. An O,O-chelating ligand, leading to a five-membered ring, is seen in **54**, Fig. 5n. In the only example of a molecule based on  $\text{Se}(=\text{O})_3$  core is the ether adduct, **55**, Fig. 5o.

## 4. One-dimensional assemblies mediated by $\text{Se}\cdots\text{O}$ chalcogen bonding

The most numerous among the supramolecular aggregation patterns described herein are one-dimensional chains. In all, 125 structures fall in this category, being over half of all examples included in this survey. The following description is based on the oxidation state of the selenium atom forming the  $\text{Se}\cdots\text{O}$  chalcogen bonding contact, the nuclearity of the molecule and the topology of the resultant chain, i.e. linear, zig-zag, helical and twisted.

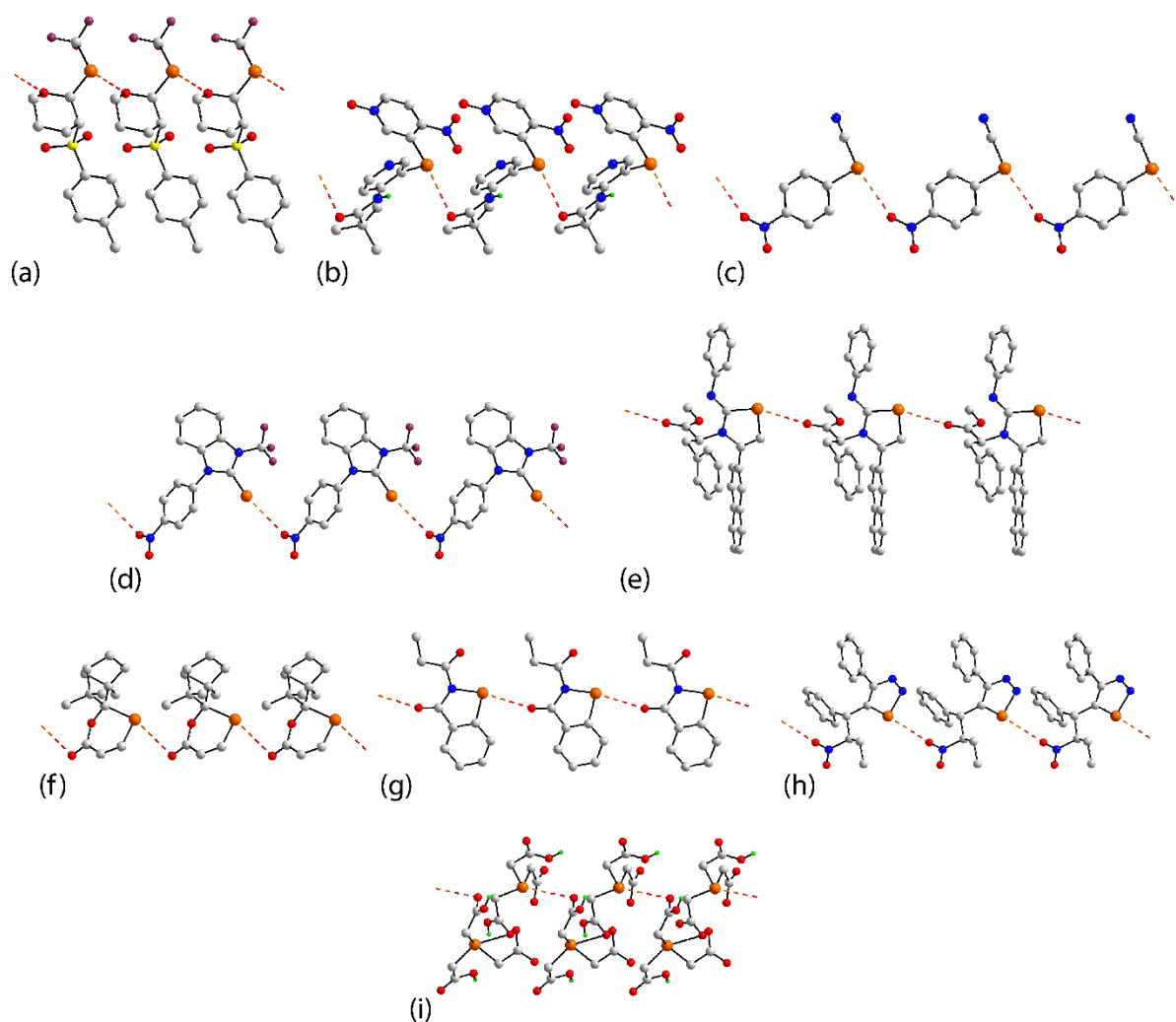
### 4.1 Mono-nuclear selenium(II) species forming linear supramolecular chains

The chemical diagrams of the 19 mono-nuclear selenium(II) molecules aggregating to form linear supramolecular chains in their crystals based on  $\text{Se}\cdots\text{O}$  chalcogen bonding contacts, i.e. **56–74** [12, 120-137], are shown in Fig. 6.



**Fig. 6.** Chemical diagrams for the interacting species, **56–74**, in selenium(II) compounds featuring  $\text{Se}\cdots\text{O}$  contacts leading to linear one-dimensional aggregates.

A variety of selenium(II) and oxygen atom environments participate in  $\text{Se}\cdots\text{O}$  contacts leading to linear, one-dimensional chains. The first six molecules have the common feature that they are diorganoselenium(II) species with the selenium atom not enclosed within a ring. Fig. 7a shows the formation of  $\text{Se}\cdots\text{O}(\text{ether})$  contacts giving rise to the chain in the crystal of **56** [120]. Molecules **57** [121], **58** [122], **59** [123] and **60** [124] employ carbonyl-oxygen atoms in the chalcogen bonding interaction. As seen in Fig. 7b for **57**,  $\text{Se}\cdots\text{O}(\text{carbonyl})$  interactions form in preference to putative  $\text{Se}\cdots\text{O}(\text{N-oxo, nitro})$  contacts. A similar situation pertains in **58** where bromide, cyano-nitrogen and two kinds of ether-oxygen atoms are available for secondary bonding interactions. The presence of  $\text{Se}\cdots\text{O}(\text{nitro})$  interactions are responsible for chain formation in the crystal of **61** [11], Fig. 7c. In **62** [125], Fig. 7d,  $\text{Se}\cdots\text{O}(\text{nitro})$  interactions are also formed. The interacting selenium atom in **62** is a rare example of a selenide forming  $\text{Se}\cdots\text{O}$  interactions, as is the case for **63** [126], which forms  $\text{Se}\cdots\text{O}(\text{methoxy})$  contacts.



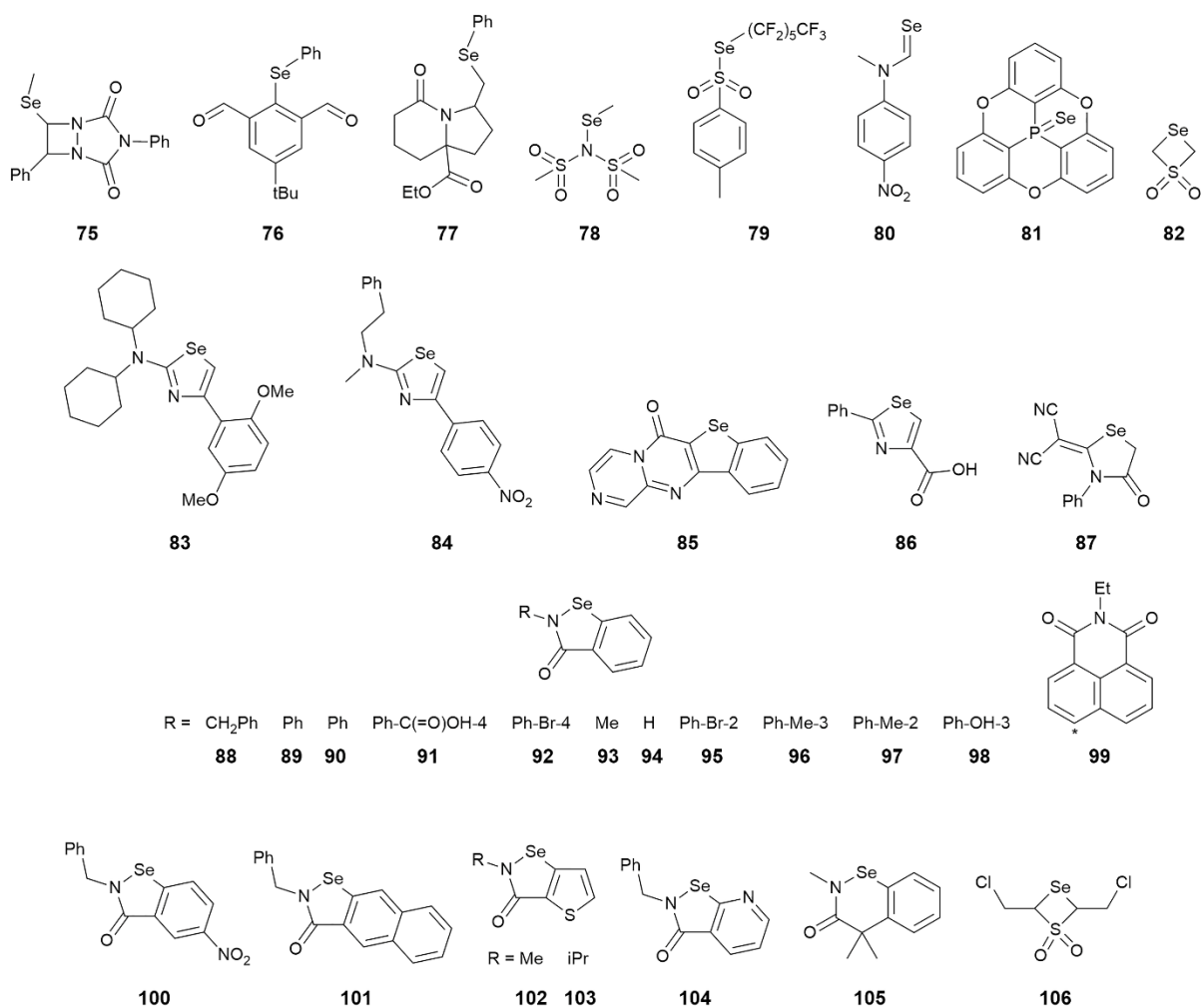
**Fig. 7.** Representative examples of supramolecular association in selenium(II) compounds leading to linear, one-dimensional chains based on  $\text{Se}\cdots\text{O}$  chalcogen bonding interactions: (a) **56** [120;  $\text{Se}\cdots\text{O} = 3.08 \text{ \AA}$ ], (b) **57** [121;  $3.12 \text{ \AA}$ ], (c) **61** [11;  $3.29 \text{ \AA}$ ], (d) **62** [125;  $3.29 \text{ \AA}$ ], (e) **64** [128;  $3.09 \text{ \AA}$ ], (f) **69** [132;  $3.39 \text{ \AA}$ ], (g) **72** [135;  $3.19 \text{ \AA}$ ], (h) **73** [136;  $3.19 \text{ \AA}$ ] and (i) **74** [137;  $3.21 \text{ \AA}$ ].

The selenium atom is incorporated within a five-membered ring and is flanked by two carbon atoms in five molecules: **64** [127], **65** [128], **66** [129], **67** [130] and **68** [131]. The  $\text{Se}\cdots\text{O}(\text{carbonyl})$  contacts in the chain formed by **64** are highlighted in Fig. 7e. The structure of **64** is notable as two independent molecules comprise the asymmetric unit and each self-assembles into a linear supramolecular chain. A similar mode association is found in the crystal

of **68**, where each of the two independent molecules self-associate into a linear chain. By contrast, in **65–67** the Se $\cdots$ O association involves ether-, methoxy- and nitro-oxygen atoms. In **69** [132], the selenium atom is incorporated within a six-membered ring and molecules assemble via Se $\cdots$ O(carbonyl) contacts, Fig. 7f. In each of the four remaining five-membered ring-containing molecules, the selenium atom is flanked by carbon and nitrogen atoms. In **70** [133], **71** [134] and **72** [135], Fig. 7g, the molecules are linked by Se $\cdots$ O(carbonyl) interactions whereas in **73** [136], Fig. 7h, Se $\cdots$ O(nitro) contacts are evident. The last structure in this category to be described is that of **74** [137] where the selenium atom formally carries a positive charge and one of three carboxylic acid substituents is deprotonated. As seen from Fig. 7i, the linear chain is sustained by Se $\cdots$ O(carbonyl) interactions; the carboxylate residue engaged is charge-assisted hydrogen bonding, precluding it from participating in Se $\cdots$ O contacts.

## 4.2 Mono-nuclear selenium(II) species forming zig-zag supramolecular chains

The chemical diagrams of the 32 mono-nuclear selenium(II) molecules, i.e. **75–106** [11, 74,101,133 138-162], forming zig-zag supramolecular chains in their crystals based on Se $\cdots$ O chalcogen bonding contacts are shown in Fig. 8. With two exceptions, as detailed below, the zig-zag chains are propagated by crystallographic glide symmetry.

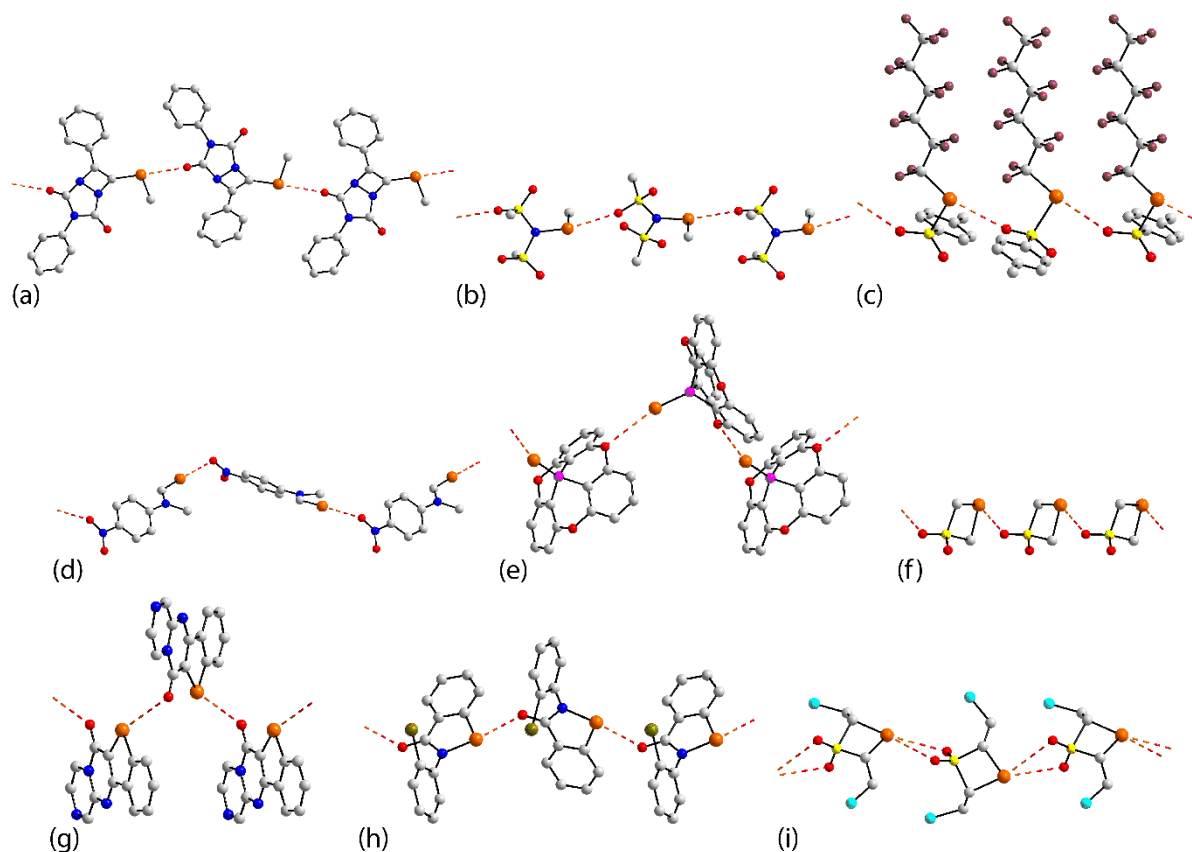


**Fig. 8.** Chemical diagrams for the interacting species, **75–106**, in selenium(II) compounds featuring Se $\cdots$ O contacts leading to zig-zag one-dimensional chains. The point of attachment at the nitrogen atom in **99** is indicated by an asterisk.

Seven compounds have the selenium atom not constrained within a ring while the remaining 25 feature cyclised selenium, usually within a five-membered ring. A representative example of a zig-zag chain is shown in Fig. 9a, for **75** [138]. Here, Se $\cdots$ O(carbonyl) interactions are in play, as in crystals of **76** [139] and **77** [140]. In **78** [141], Fig. 7b, an example rich in heteroatoms, Se $\cdots$ O(sulphoxide) interactions are evident, as they are in **79** [142], Fig. 9c, with a rare C,S-donor set for selenium. The structures of **80** [143] and **81** [144] are examples of selenides are engaged in Se $\cdots$ O interactions. In **80**, there are two independent molecules in the



asymmetric unit and each of these self-associates into a supramolecular chain via  $C=Se\cdots O(\text{nitro})$  interactions, one of these is shown in Fig. 9d. In **81**, where the selenide is phosphorus-bound, the zig-zag chain, Fig. 9e, arises as a result of  $P=S\cdots O(\text{ether})$  contacts. The remaining molecules to be covered have the selenium atom incorporated with a ring.



**Fig. 9.** Representative examples of supramolecular association in selenium(II) compounds leading to linear, one-dimensional chains based on  $Se\cdots O$  chalcogen bonding interactions: (a) **75** [138;  $Se\cdots O = 3.05 \text{ \AA}$ ], (b) **77** [140;  $3.06 \text{ \AA}$ ], (c) **78** [141;  $3.16 \text{ \AA}$ ], (d) **80** [143;  $3.12 \text{ \AA}$ ], (e) **81** [144;  $3.41 \text{ \AA}$ ], (f) **82** [74;  $3.05 \text{ \AA}$ ], (g) **85** [101;  $3.36 \text{ \AA}$ ], (h) **95** [154;  $2.67 \text{ \AA}$ ], (i) **106** [163;  $3.29 \text{ \AA}$  &  $3.35 \text{ \AA}$ ].

In the next six molecules, each selenium(II) atom has a C,C-donor set. The selenium atom in **82** [74] forms part of a four-membered ring and the molecules assemble into a zig-zag chain via  $Se\cdots O(\text{sulphoxide})$  contacts, Fig. 9f. The chains in **83** [145] are sustained by

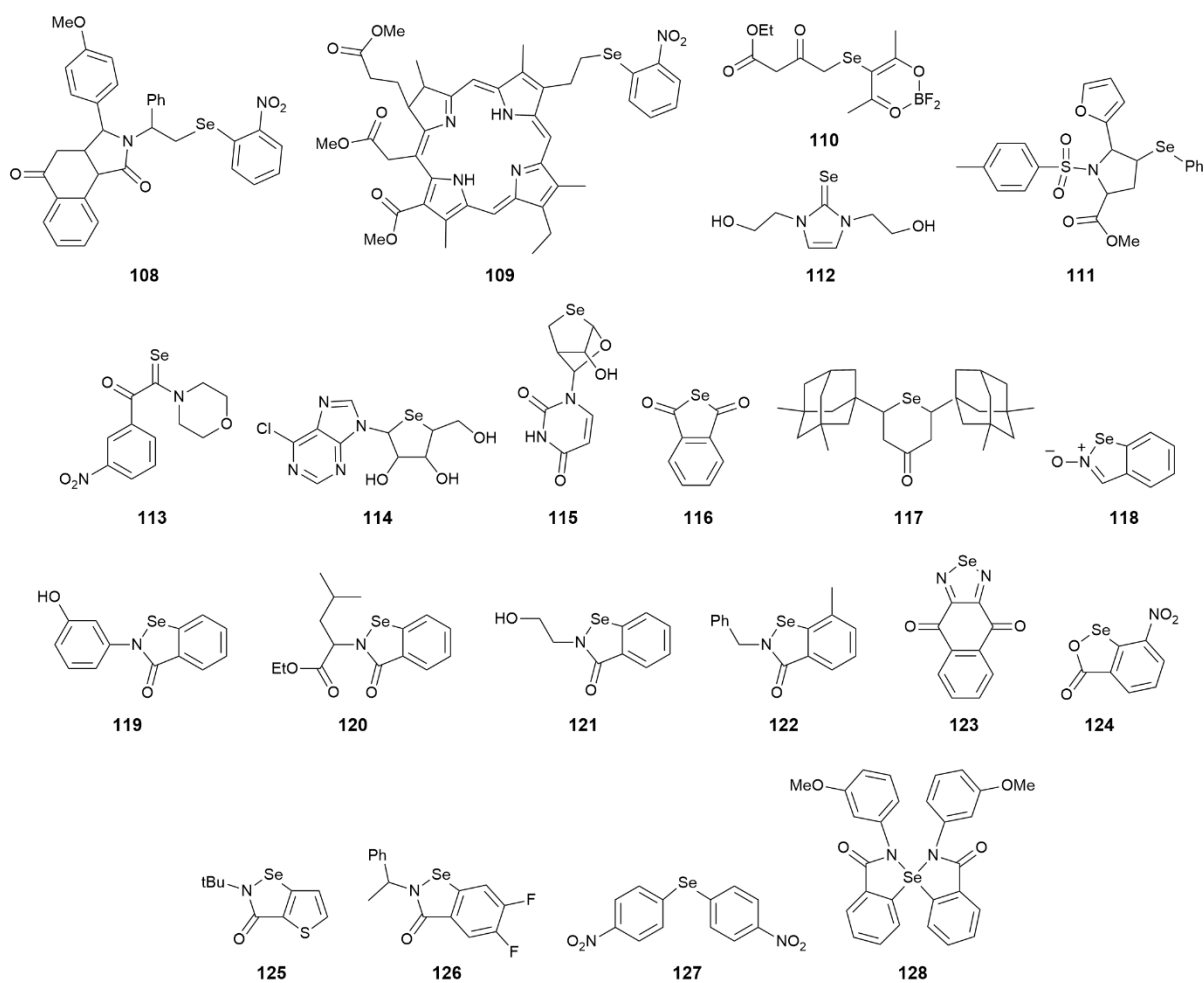
Se $\cdots$ O(methoxy) interactions, and in **84** [146], **85** [101], **86** [147] and **87** [148] by Se $\cdots$ O(carbonyl) interactions. Compound **85** is one of two molecules in this section assembling into a zig-zag chain not propagated by glide symmetry. In this case, there are two independent molecules which associate to form the supramolecular chain.

Next, is a series of molecules constructed about a 5-selanylidene-1H-pyrrol-2-one core, i.e. **88–99** [11, 149-157], featuring a variety of substituents, R, at the nitrogen atom: R = CH<sub>2</sub>Ph (**88**) [149], Ph, polymorphs **89** [11] and **90** [150], Ph-C(=O)OH-4 (**91**) [151], Ph-Br-4 (**92**) [152], Me (**93**) [153], H, acid **94** [152], Ph-Br-2 (**95**) [154], Ph-Me-3 (**96**) [155], Ph-Me-2 (**97**) [156], Ph-OH-3 (**98**) [11] and, lastly, R = a fused 1-ethylpiperidine-2,6-dione/naphthalene derivative (**99**) [157]. The common mode of the supramolecular association is the formation of Se $\cdots$ O(carbonyl) interactions, as illustrated for **95** [154] in Fig. 9h. Generally, these contacts are short, ranging from 2.53 Å in **88** [149] to 2.86 Å for **99** [157], suggesting considerable covalent character in these secondary bonding interactions. As indicated above, **89** and **90** are polymorphs. These exhibit the same supramolecular aggregation via Se $\cdots$ O(carbonyl) interactions with very similar Se $\cdots$ O separations of 2.53 and 2.57 Å, respectively. Of interest is the R = H derivative, **94**, i.e. the acid form, where three independent molecules comprise the asymmetric unit. One molecule self-assembles into a zig-zag chain (glide symmetry). The two other molecules associate via a Se $\cdots$ O(carbonyl) interaction and the resultant dimeric aggregates assemble into a zig-zag chain, again propagated by glide symmetry. Variations of the above are seen in **100** [133], where the fused C<sub>6</sub> ring carries a nitro substituent, and **101** [158], where the fused C<sub>6</sub> ring is fused to a second C<sub>6</sub> ring, and in **102** and **103** [159], where the fused C<sub>6</sub> ring is substituted by a thienyl ring; each of the resultant zig-zag chains are sustained by Se $\cdots$ O(carbonyl) interactions. The Se $\cdots$ O(carbonyl) interactions persist in **104** [160], where the fused C<sub>6</sub> ring is now a pyridyl ring and **105** [161], where the selenium atom is incorporated into a six-membered ring. The final molecule in this section, **106** [162], Fig.

9i, is notable in that the selenium atom, embedded within a four-membered ring, forms two  $\text{Se}\cdots\text{O}$ (sulphoxide) interactions to sustain the zig-zag chain.

### 4.3 Mono-nuclear selenium(II) species forming helical and twisted supramolecular chains

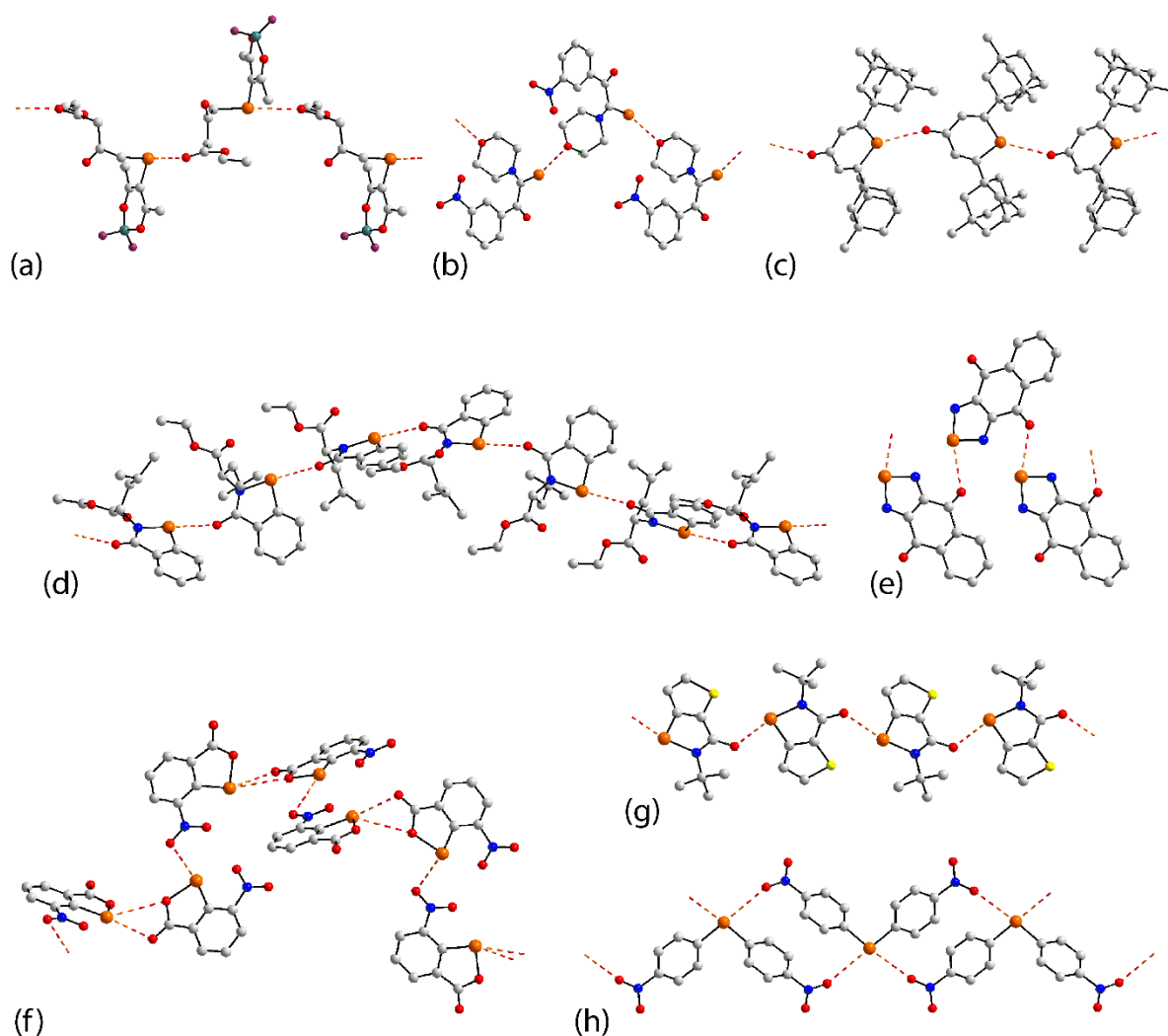
The chemical diagrams of the mono-nuclear selenium(II) molecules, i.e. **107–123** [152,163-177] and **124–126** [159,178,179], forming, respectively, helical and twisted supramolecular chains in their crystals based on  $\text{Se}\cdots\text{O}$  chalcogen bonding contacts are shown in Fig. 10.



**Fig. 10.** Chemical diagrams for the interacting species, **107–123**, in selenium(II) compounds featuring Se $\cdots$ O contacts leading to helical one-dimensional chains, and **124–126**, leading to twisted chains.

The supramolecular chains with helical symmetry are typically propagated by crystallographic 2<sub>1</sub> screw symmetry, with two exceptions only, and, while less numerous than zig-zag supramolecular chains sustained by Se $\cdots$ O interactions, comprise 17 examples. Six of the molecules do not have selenium incorporated within a ring, and four of these have selenium within a C<sub>2</sub>-donor set: **107** [163], **108** [164], **109** [165], Fig. 10a, and **110** [166], and two of the examples are selenides **111** [167] and **112** [168], Fig. 10b. Highlighting the diversity of oxygen-donors in these chains, in **107** and **109** they feature Se $\cdots$ O(carbonyl) contacts, **108** Se $\cdots$ (methoxy), **110** Se $\cdots$ O(sulphoxide), **111** Se $\cdots$ O(hydroxyl) and the chains in **112** are sustained by Se $\cdots$ O(ether) interactions. The remaining helical structures feature cyclised selenium atoms. The five-membered rings in **113** [169], **114** [170] and **115** [171] also feature C<sub>2</sub> donor sets as does the selenium atom in **116** [172], Fig. 10c, which is now incorporated within a six-membered ring. The donor atoms forming the Se $\cdots$ O interactions are hydroxyl in **113** but, carbonyl in **114–116**; in **114**, both ether and hydroxyl donors are available but not employed in Se $\cdots$ O contacts. The remaining ring structures contain hetero-atoms, all having at least one nitrogen atom, with two exceptions. In **117** [173], the helical chain is sustained by a charge-assisted Se $\cdots$ O(N-oxo) interaction with the separation being a short 2.41 Å. Molecules **118** [152], **119** [174], **120** [152] and **121** [175] all feature the 5-selanylidene-1H-pyrrol-2-one core, as seen above in the sequence of molecules **88–99**. The chains in **118** and **120** are sustained by Se $\cdots$ O(hydroxyl) interaction despite having potential carbonyl donors, whereas the chains in **119** and **121** feature Se $\cdots$ O(carbonyl) interactions. It is noted that **118** has two polymorphs: in **5**, Fig. 3a, the two independent molecules of the asymmetric unit assemble by

a single Se $\cdots$ O(carbonyl) interaction and in second polymorph, **98**, molecules assemble into a zig-ag chain, but via Se $\cdots$ O(hydroxyl) interactions as in **118**. The helical chain formed in **119** is especially noteworthy in that rather than the usually observed 2<sub>1</sub> symmetry, the chain is propagated by crystallographic 6<sub>1</sub> screw symmetry, Fig. 10d. In **122** [176], where there are two nitrogen atoms in the ring, flanking the selenium atom, the helical chain is sustained by Se $\cdots$ O(carbonyl) interactions, Fig. 10e. The supramolecular aggregation in **123** [177] is quite unusual, featuring three distinct Se $\cdots$ O contacts for the selenium atoms derived from the two independent molecules comprising the asymmetric unit. As viewed from Fig. 10f, one selenium atom forms a single contact with a nitro-oxygen atom while the other selenium atom spans the two oxygen atoms of a symmetry related five-membered ring. The shortest Se $\cdots$ O contact of 2.90 Å in the chain is associated with the Se $\cdots$ O(carbonyl) interaction. The other unusual feature of the resulting supramolecular chain is that it is propagated by crystallographic 4<sub>1</sub> screw symmetry.



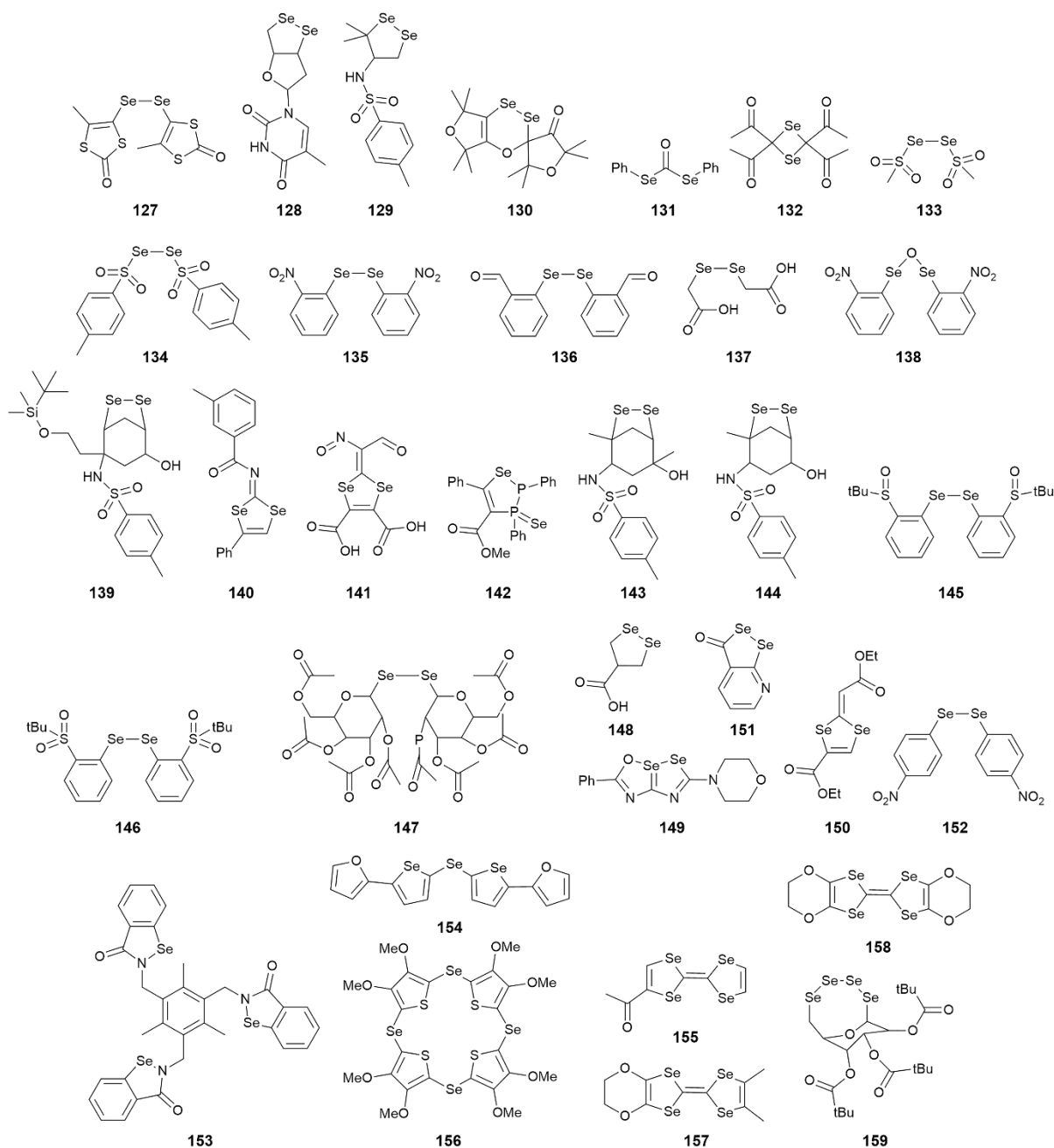
**Fig. 11.** Representative examples of supramolecular association in selenium(II) compounds leading to helical, one-dimensional chains based on  $\text{Se}\cdots\text{O}$  chalcogen bonding interactions: (a) **109** [165;  $\text{Se}\cdots\text{O} = 3.04 \text{ \AA}$ ], (b) **112** [168;  $3.39 \text{ \AA}$ ], (c) **116** [172;  $3.18 \text{ \AA}$ ], (d) **119** [174;  $2.83 \text{ \AA}$ ], (e) **122** [176;  $2.95 \text{ \AA}$ ], (f) **123** [177;  $2.90, 3.30 \text{ \AA}$  &  $3.38 \text{ \AA}$ ], (g) **125** [159;  $2.55 \text{ \AA}$ ] and (h) **126** [179;  $3.26 \text{ \AA}$ ]. Additional colour code: teal, boron.

There are three molecules, **124** [159], **125** [178] and **126** [179], assembling in their crystals to form twisted chains. In **124**, Fig. 10g, and **125**, two independent molecules comprise the asymmetric unit with the twisted arrangement arising due to the relative orientations of the independent molecules in the chains propagated by translational symmetry; chains are

sustained by Se $\cdots$ O(carbonyl) contacts. The molecule in **126**, Fig. 10h, has crystallographic two-fold symmetry with the selenium atom lying on the axis. Each selenium atom forms two Se $\cdots$ O(nitro) contacts with centrosymmetrically related molecules.

#### **4.4 Multi-nuclear selenium(II) species forming supramolecular chains**

Most of the molecules in this category are bi-nuclear but, there are several examples of tri- and tetra-nuclear selenium(II) compounds. The chemical structures for the molecules forming the supramolecular chains, i.e. **127–159** [80,92,95,104,180-205], are shown in Fig. 11.



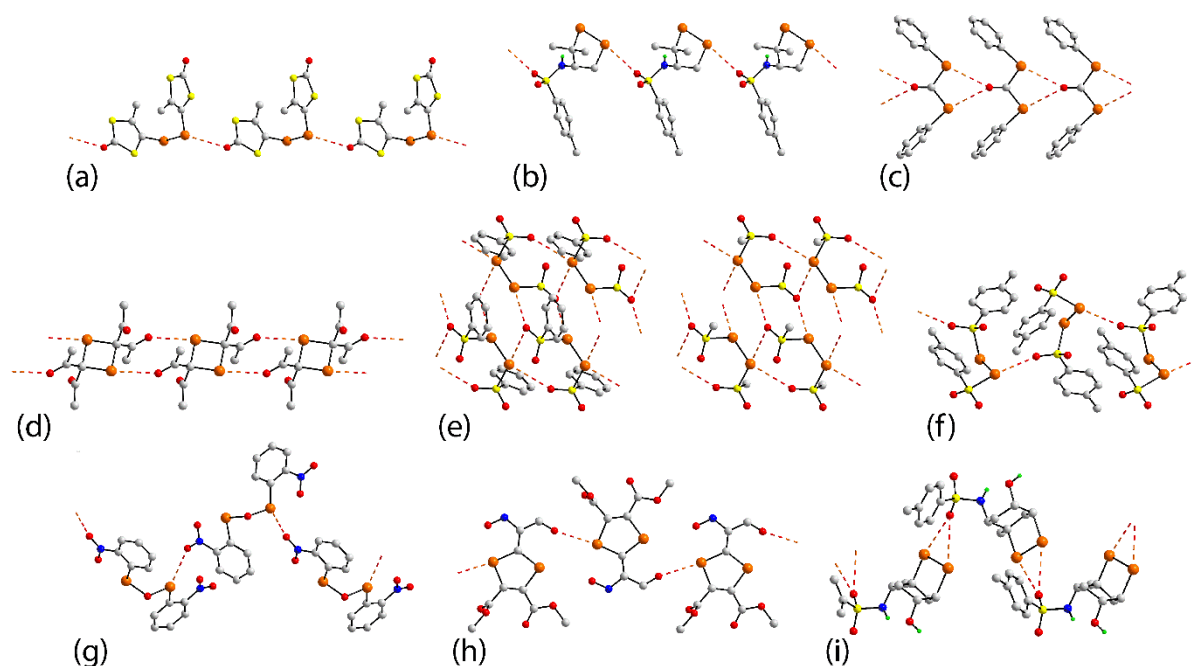
**Fig. 12.** Chemical diagrams for the interacting species, **127–159** [80,95,152,159,180-205], in multi-nuclear selenium(II) compounds featuring  $\text{Se}\cdots\text{O}$  contacts leading to supramolecular one-dimensional chains.

#### 4.4.1 Bi-nuclear selenium(II) species forming linear chains

A linear chain is observed in crystals of **127** [180], Fig. 13a, an example whereby the selenium atom is not embedded within a ring, and where only one of the selenium atoms is



engaged in a Se $\cdots$ O contact, in this case where the donor is a carbonyl-oxygen atom. When embedded within a five-membered ring, the selenium atoms can be next to each other as in **128** [181] and **129** [182], Fig. 10b, or in a six-membered ring, i.e. **130** [183]. Again, only one of the selenium atoms in **128–130** forms a Se $\cdots$ O contact, with the donors being ether-, sulphoxide- and carbonyl-oxygen, respectively. The structure of **129** is especially noteworthy in that two molecules comprise the asymmetric unit, and these possess amide donors capable of forming hydrogen bonding interactions. One of the independent molecules forms a supramolecular chain, as just mentioned, and these are connected into a double-chain by conventional amide-N–H $\cdots$ O(sulphoxide) hydrogen bonds involving the same sulphoxide-oxygen atom forming the Se $\cdots$ O contacts. The second independent molecule also forms a supramolecular chain but, mediated solely by amide-N–H $\cdots$ O(sulphoxide) hydrogen bonds, there being no Se $\cdots$ O interactions of note. The adoption of Se $\cdots$ O and/or amide-N–H $\cdots$ O(sulphoxide) hydrogen bonds suggests, at least to a first approximation, some equivalence in the energies of stabilisation afforded by these modes of association. In **131** [184], the association leading to a linear chain involves both selenium atoms connecting to the carbonyl-oxygen atom of a translationally related molecule, Fig. 13c. A double-chain is noted for **132** [185], Fig. 13d. Here, two selenium atoms occur diagonally opposite positions in a centrosymmetric C<sub>2</sub>Se<sub>2</sub> square, and each forms a Se $\cdots$ O(carbonyl) interaction to form a linear chain. Two independent molecules also comprise the asymmetric unit of **133** [186]. One of these self-associates into a linear chain via Se $\cdots$ O(sulphoxide) contacts whereby one selenium atom forms two contacts with translationally related molecules leading to seven-membered { $\cdots$ Se $\cdots$ OSSeSeSO} synthons. Centrosymmetrically related chains assemble into a double-chain, also via Se $\cdots$ O(sulphoxide) contacts, but involving the second selenium atom (forming the shortest Se $\cdots$ O contact) and six-membered { $\cdots$ OSSe}<sub>2</sub> synthons, as shown in the views of Fig. 13e.



**Fig. 13.** Representative examples of supramolecular association in selenium(II) compounds leading to helical, one-dimensional chains based on  $\text{Se}\cdots\text{O}$  chalcogen bonding interactions: (a) **127** [180;  $\text{Se}\cdots\text{O} = 3.29 \text{ \AA}$ ], (b) **129** [182;  $3.22 \text{ \AA}$ ], (c) **131** [184;  $3.35 \text{ \AA}$ ], (d) **132** [185;  $3.04 \text{ \AA}$ ], (e) **133** and view with only ipso-carbon atoms [186;  $3.09, 3.37 \text{ \AA}$  &  $3.35 \text{ \AA}$ ], (f) **136** [189;  $3.03 \text{ \AA}$ ], (g) **138** [95;  $3.25 \text{ \AA}$ ], (h) **141** [192;  $3.05 \text{ \AA}$ ] and (i) **144** [190;  $3.18 \text{ \AA}$  &  $3.36 \text{ \AA}$ ].

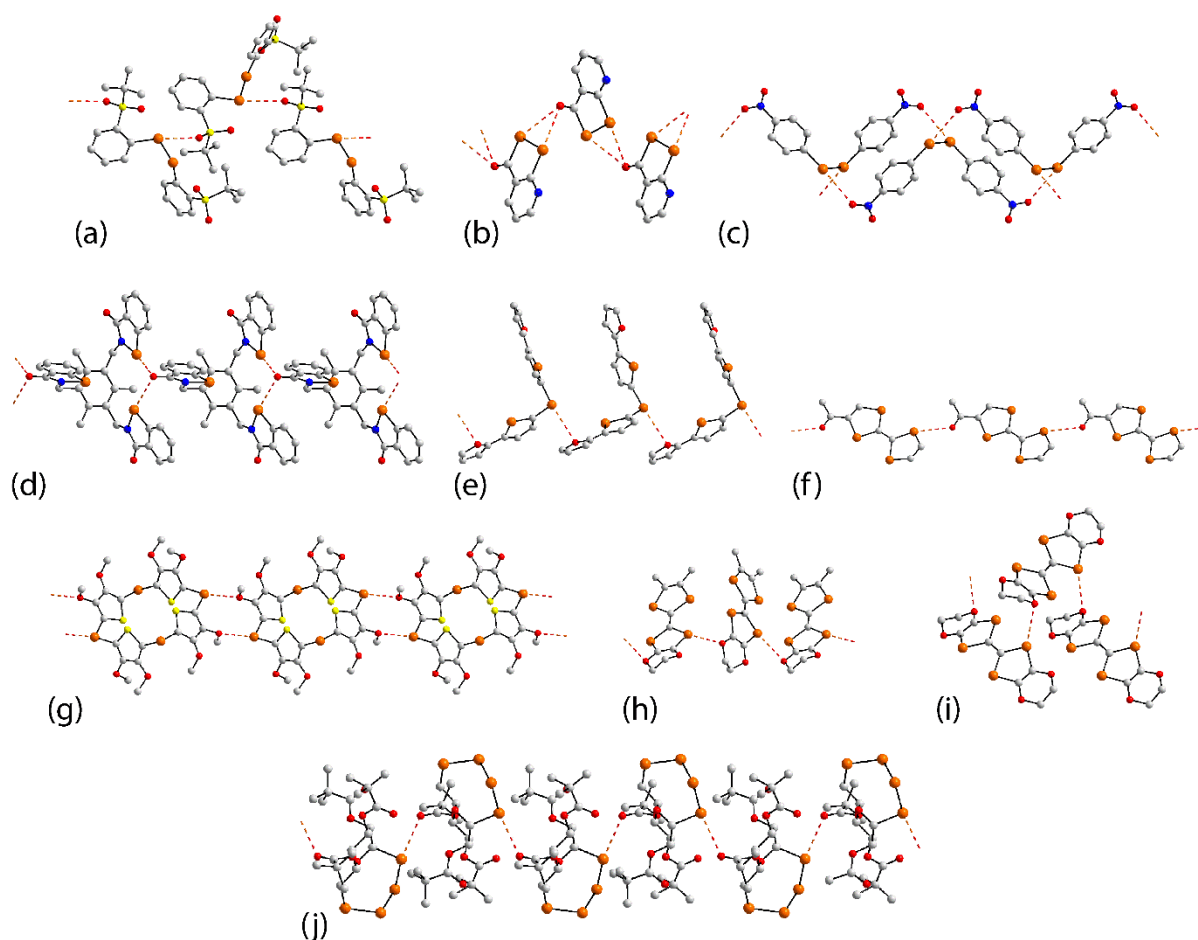
#### 4.4.2 Bi-nuclear selenium(II) species forming zig-zag chains

Four molecules of the general formula  $\text{RSeSeR}$  form supramolecular zig-zag chains in their crystals; these along with the other chains described in this section are propagated by glide symmetry. These are sustained by an average of one  $\text{Se}\cdots\text{O}(\text{sulphoxide})$  contact per molecule in **134** [186], Fig. 13f,  $\text{Se}\cdots\text{O}(\text{nitro})$  in **135** [187] and  $\text{Se}\cdots\text{O}(\text{carbonyl})$  in each of **136** [188] and **137** [189]. A variation is noted for **138** [95], Fig. 13g, where the selenium atoms are connected by an oxo bridge and one of these forms  $\text{Se}\cdots\text{O}(\text{nitro})$  contacts. The selenium atoms are adjacent to each other in the five-membered ring of **139** [190] and one of these participates in  $\text{Se}\cdots\text{O}(\text{sulphoxide})$  interactions to form the zig-zag chain. In the five-membered rings of each

of **140** [191] and **141** [192], Fig. 13h, the selenium atoms are separated by a carbon atom, and the chain is mediated by  $\text{Se}\cdots\text{O}(\text{carbonyl})$  interactions. In **142** [80],  $\text{Se}\cdots\text{O}(\text{hydroxyl})$  interactions involving the ring-bound selenium atom mediate the formation of the zig-zag chain rather than putative interactions involving the phosphorus-bound selenide atom. A variation in the general theme of one  $\text{Se}\cdots\text{O}$  link per molecule to sustain the zig-zag chain is noted for **143** and **144** [190], Fig. 13i, where each selenium atom, occupying adjacent positions in a five-membered ring, participates in  $\text{Se}\cdots\text{O}(\text{sulphoxide})$  interactions with the same sulphoxide-oxygen atom.

#### 4.4.3 Bi-nuclear selenium(II) species forming helical chains

The common feature of the seven helical chains formed by bi-nuclear selenium(II) molecules is that each is propagated by  $2_1$  screw symmetry. The first six molecules employ a single selenium atom in forming the  $\text{Se}\cdots\text{O}$  chalcogen bond: **145**, **146** [193], Fig. 14a, **147** [194], **148** [195], **149** [196] and **150** [197]. The oxygen donors span a range of types, i.e. sulphoxide (**145** and **146**), ether (**147**) and carbonyl (**148** and **150**) and phenoxide (**149**). In **151** [198], Fig. 14b, the adjacent selenium atoms are embedded within a five-membered ring and form contacts to the same carbonyl-oxygen atom to form the helical chain, i.e. bearing a close resemblance to the aggregation pattern seen in **143** and **144**, Fig. 13i. The bi-molecule in **152** [199], has two-fold symmetry with the axis bisecting the Se–Se bond, and each selenium atom forms a  $\text{Se}\cdots\text{O}(\text{nitro})$  contact to a centrosymmetrically related molecule with the result a twisted chain ensues, Fig. 14c.



**Fig. 14.** Representative examples of supramolecular association in multi-nuclear selenium(II) compounds leading to one-dimensional chains of varying topology based on  $\text{Se}\cdots\text{O}$  chalcogen bonding interactions: (a) **146** [193;  $\text{Se}\cdots\text{O} = 3.19 \text{ \AA}$ ], (b) **151** [198;  $3.24 \text{ \AA}$  &  $3.24 \text{ \AA}$ ], (c) **152** [199;  $3.22 \text{ \AA}$ ], (d) **153** [152;  $2.99 \text{ \AA}$  &  $3.12 \text{ \AA}$ ], (e) **154** [200;  $3.34 \text{ \AA}$ ], (f) **155** [201;  $3.22 \text{ \AA}$ ], (g) **156** [202;  $3.03 \text{ \AA}$ ], (h) **157** [203;  $3.13 \text{ \AA}$ ], (i) **158** [204;  $3.35 \text{ \AA}$ ] and (j) **159** [205;  $3.16 \text{ \AA}$  &  $3.17 \text{ \AA}$ ].

#### 4.4.4 Multi-nuclear selenium(II) species forming supramolecular chains

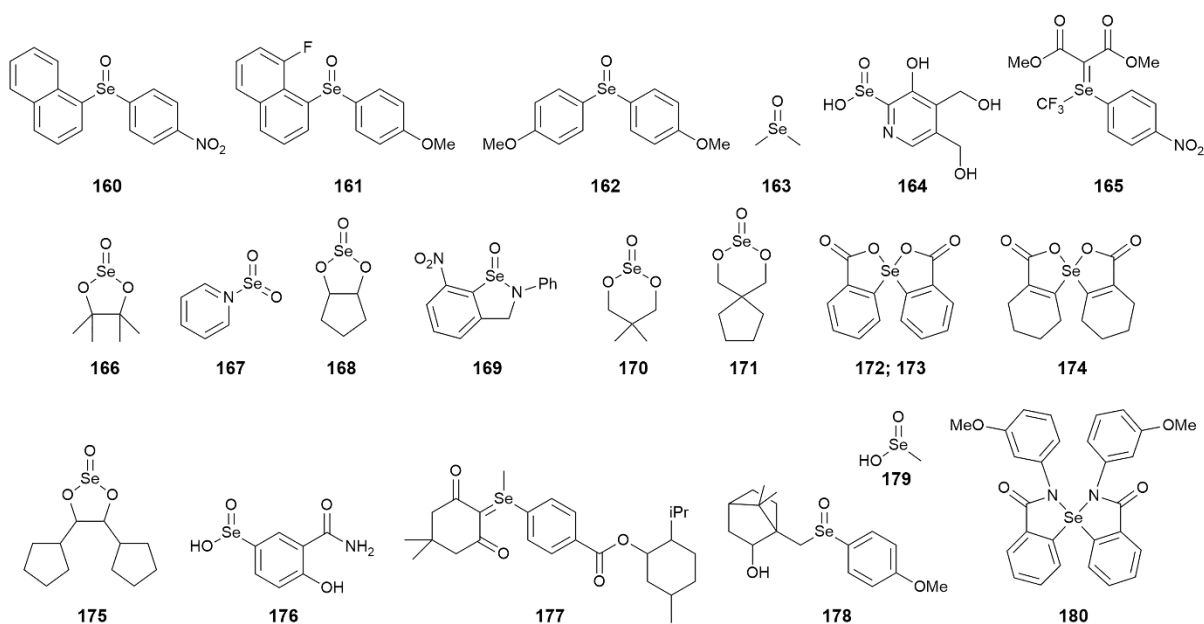
There are two tri-nuclear selenium(II) species forming supramolecular chains in their crystals. As a result of  $\text{Se}\cdots\text{O}(\text{carbonyl})$  interactions whereby two of the three selenium atoms, each within a five-membered ring, form a contact to the same carbonyl-oxygen atom, a linear chain is formed in the crystal of **153** [152], Fig. 14d. In **154** [200], where there is an “open”

selenium atom and two selenium atoms within five-membered rings, it is the former that forms a  $\text{Se}\cdots\text{O}(\text{ether})$  contact to generate a zig-zag chain via glide symmetry, Fig. 14e.

The remaining five selenium(II)-containing species in this section are tetra-nuclear. In **155** [201], two five-membered rings, each with a 1,3-disposition of selenium atoms, are connected to form the tetra-nuclear molecule. In the crystal, only one of the selenium atoms forms a  $\text{Se}\cdots\text{O}(\text{carbonyl})$  interaction with translationally related molecules so that a linear chain is formed, Fig. 14f. The macrocyclic compound, **156** [202], employs two of its selenium atoms to sustain a linear assembly via  $\text{Se}\cdots(\text{methoxy})$  interactions and eight-membered  $\{\cdots\text{SeC}_2\text{O}\}_2$  synthons, Fig. 14g. The molecule **157** [203] is clearly related to **155** but, in this case, this assembles into a zig-zag chain (glide symmetry), Fig. 14h. The remaining molecules, **158** [204], and **159** [205], assemble into helical chains, for **158**, Fig. 14i, propagated by  $2_1$  screw symmetry. An interesting variation is noted for **159** in that the four selenium atoms line up in a chain within an eight-membered ring; two independent molecules comprise the asymmetric unit. The independent molecules assemble via a  $\text{Se}\cdots\text{O}(\text{carbonyl})$  contact and the resultant dimeric aggregate then assembles, via additional  $\text{Se}\cdots\text{O}(\text{carbonyl})$  contacts, into a supramolecular helical chain propagated by  $3_1$  screw symmetry, Fig. 14j.

#### 4.5 Multi-nuclear selenium(IV) species forming supramolecular chains

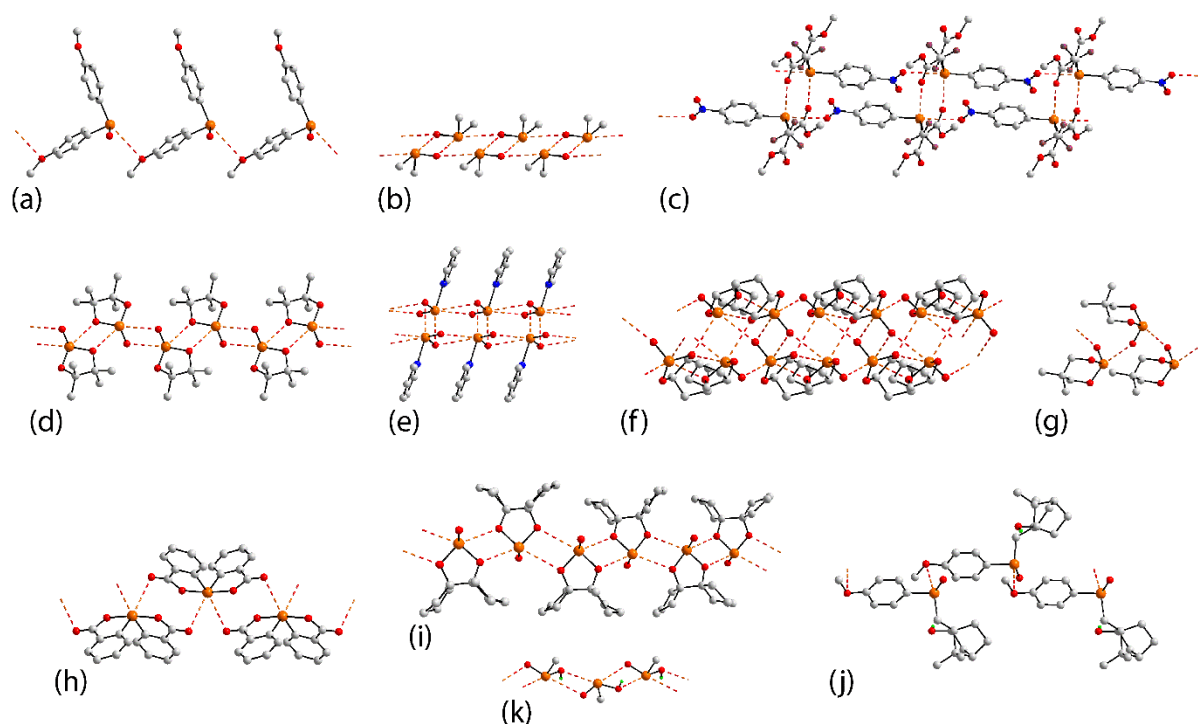
While far less represented than their selenium(II) counterparts, there are 21 examples of selenium(IV) compounds, usually selenoxide derivatives, self-associating in their crystals to form one-dimensional chains via  $\text{Se}\cdots\text{O}$  chalcogen bonding. The chemical diagrams for these, i.e. **160–180** [93,104,105,113,188,206-217], are shown in Fig. 15.



**Fig. 15.** Chemical diagrams for the interacting species, **160–180**, in selenium(IV) compounds featuring  $\text{Se}\cdots\text{O}$  contacts leading to supramolecular one-dimensional chains.

The three selenoxides, **160** [104], **161** [104] and **162** [206], Fig. 16a, feature  $\text{C}_2\text{O}$ -donor sets and associate in their crystals to form linear, supramolecular chains via  $\text{Se}\cdots\text{O}(\text{nitro})$  interactions in **160**, and  $\text{Se}\cdots\text{O}(\text{methoxy})$  interactions in **161** and **162**. Double-chains are often observed in the crystals of the selenium(IV) compounds in this category owing to the formation of multiple  $\text{Se}\cdots\text{O}$  interactions. This is exemplified by **163** [207], Fig. 16b. Here, centrosymmetrically related molecules are connected by a pair of  $\text{Se}\cdots\text{O}(\text{oxide})$  interactions, leading to a  $\{\cdots\text{Se}-\text{O}\}_2$  core, and the resultant dimeric aggregates assemble into a linear, double-chain so each selenium atom forms two  $\text{Se}\cdots\text{O}$  contacts. Similar patterns are noted in **164** [208], Fig. 16c, and **165** [209] but, with the bridges leading to the chains being interactions of the type  $\text{Se}\cdots\text{O}(\text{nitro})$ ; in **164**, the  $\text{Se}\cdots\text{O}(\text{carbonyl})$  separations are shorter than the  $\text{Se}\cdots\text{O}(\text{nitro})$  contacts whereas the opposite trend pertains in **165**, underscoring the difficulty of correlating distances associated with weak interactions as discussed in section 8. In **166** [210], Fig. 16d, with a chelating  $\text{O},\text{O}$ -ligand leading to a five-membered ring, the double-chain arises

as the successive, centrosymmetrically related aggregates are connected by  $\text{Se}\cdots\text{O}(\text{alkoxide})$  interactions. In the dioxide species, **167** [211], Fig. 16e, the centrosymmetric aggregates are connected to translationally related dimers via a pair of  $\text{Se}\cdots\text{O}(\text{oxide})$  contacts so each selenium atom participates in three  $\text{Se}\cdots\text{O}$  interactions. A more complicated mode of association between molecules occurs in **168** [113], Fig. 16f, for which two independent molecules comprise the asymmetric unit. One of the independent molecules assembles to form a dimer and translationally related dimers are bridged by a pair of the second independent molecule. There are six independent  $\text{Se}\cdots\text{O}$  contacts involving oxide- (4) and alkoxide-oxygen (2) donors, and each selenium atom participates in three  $\text{Se}\cdots\text{O}$  interactions.



**Fig. 16.** Representative examples of supramolecular association in multi-nuclear selenium(II) compounds leading to one-dimensional chains of varying topology based on  $\text{Se}\cdots\text{O}$  chalcogen bonding interactions: (a) **162** [206;  $\text{Se}\cdots\text{O} = 3.37 \text{ \AA}$ ], (b) **163** [207;  $3.24 \text{ \AA}$  &  $3.32 \text{ \AA}$ ], (c) **165** [209;  $3.14 \text{ \AA}$  &  $3.22 \text{ \AA}$ ], (d) **166** [210;  $2.89 \text{ \AA}$  &  $2.93 \text{ \AA}$ ], (e) **167** [211;  $3.00 \text{ \AA}$ ,  $3.26 \text{ \AA}$  &  $3.29 \text{ \AA}$ ], (f) **168**

[113; 2.69-3.20 Å], (g) **170** [113; 2.78 Å], (h) **173** [212; 3.22 Å], (i) **175** [113; 2.84-3.21 Å], (j) **179** [217; 3.40 Å] and (k) **179** [216; 3.16 & 3.31 Å].

Molecules **169** [93], **170** [113], Fig. 16g, and **171** [113], each with C<sub>2</sub>O donor sets, assemble into zig-zag chains mediated by a single Se $\cdots$ O(oxide) contact in each case. In **171**, two independent molecules comprise the asymmetric unit and these are connected by a single Se $\cdots$ O(oxide) interaction and these dimers then assemble into a zig-zag chain via additional Se $\cdots$ O(oxide) interactions. Compounds **172** [188] and **173** [212], in which the selenium centres are O,O-chelated by two chelating ligands, are polymorphic. In **172**, a single Se $\cdots$ O(carbonyl) interaction, on average, sustains a zig-zag assembly (glide symmetry). By contrast, in **173**, Fig. 16h, the selenium atom lies on a two-fold axis of symmetry and there are, on average two Se $\cdots$ O(carbonyl) interactions per molecule with the Se $\cdots$ O(carbonyl) distance of 3.22 Å being longer than 3.02 Å observed in **172**, as would be expected. The molecule in **174** [213], also has the selenium atom lying on a two-fold axis of symmetry and a similar mode of association as for **173** is noted in its crystal. The supramolecular association **175** [113] is of particular interest. Here, there are four independent molecules in the asymmetric unit and each participates in Se $\cdots$ O contacts. Two of the independent molecules assemble into a tetrameric aggregate via Se $\cdots$ O(oxide) and Se $\cdots$ O(alkoxide) interactions as shown for aggregate **48** [113] in Fig. 5h. In the second assembly found in the crystal of **175**, involving the two remaining independent molecules, only Se $\cdots$ O(alkoxide) interactions are formed leading to a zig-zag chain with each selenium atom forming two Se $\cdots$ O interactions, Fig. 16i.

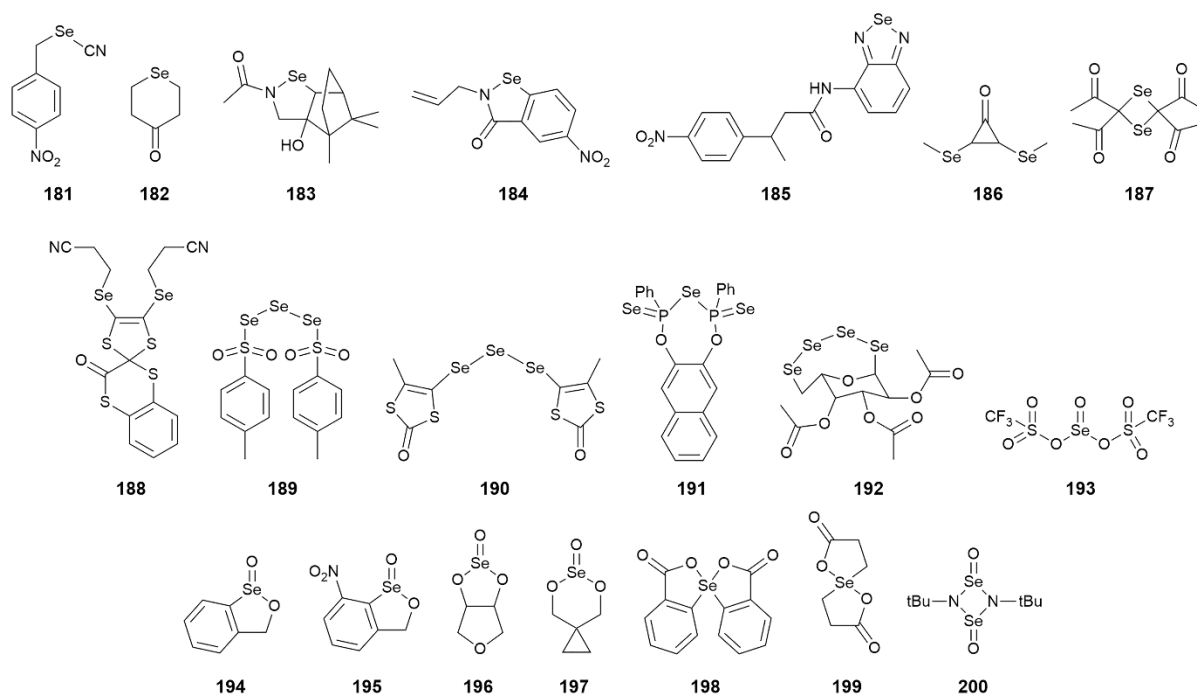
Helical chains (2<sub>1</sub> screw symmetry) are found in crystals of **176** [105], **177** [214] and **178** [215], Fig. 16j, sustained by either Se $\cdots$ O(carbonyl), **176** and **177**, or Se $\cdots$ O(methoxy), **178**, interactions. A helical chain, also with 2<sub>1</sub> screw symmetry, occurs in the crystal of **179** [216], Fig. 16k, as the selenium atom accepts bond Se $\cdots$ O(oxide) and Se $\cdots$ O(hydroxyl) interactions,



rather than the single Se...O interactions of the previous three examples. Finally, in **180** [217] two independent molecules comprise the asymmetric unit and each selenium atom participates in two Se...O(carbonyl) interactions with the chain, propagated by translational symmetry, having a twisted topology owing to the relative orientation of the independent molecules comprising the repeat unit.

## 5. Two-dimensional assemblies mediated by Se...O chalcogen bonding

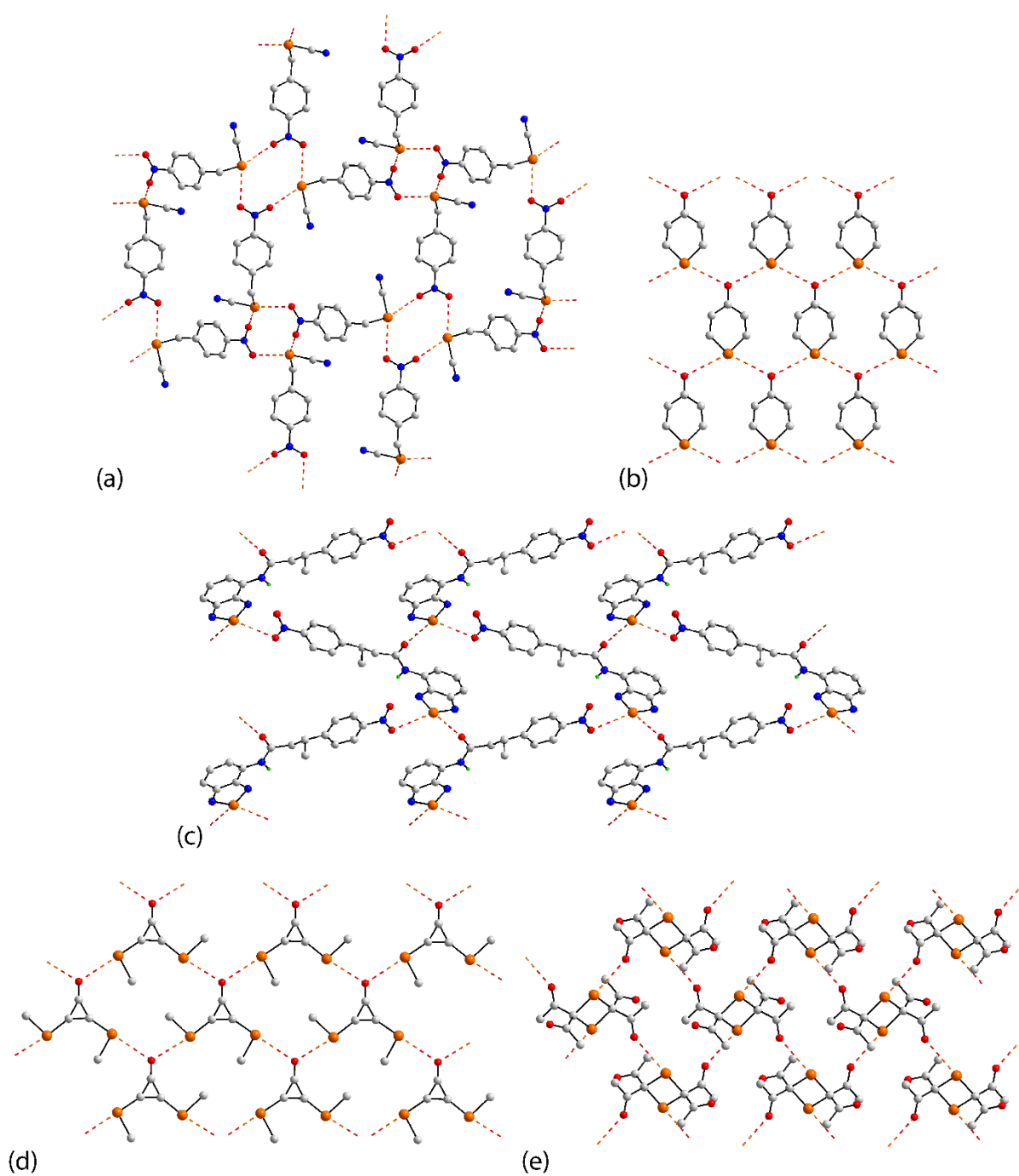
When Se...O chalcogen bonding extends in two dimensions, supramolecular layers are formed: this has been noted in a total of 20 crystals, with 12 selenium(II) and eight selenium(IV) examples. The chemical diagrams for **181–200** [95,113,133,186,218-231] are shown in Fig. 17.



**Fig. 17.** Chemical diagrams for the interacting species, **181–200**, in selenium(II) and selenium(IV) compounds featuring Se...O contacts leading to supramolecular, two-dimensional arrays.

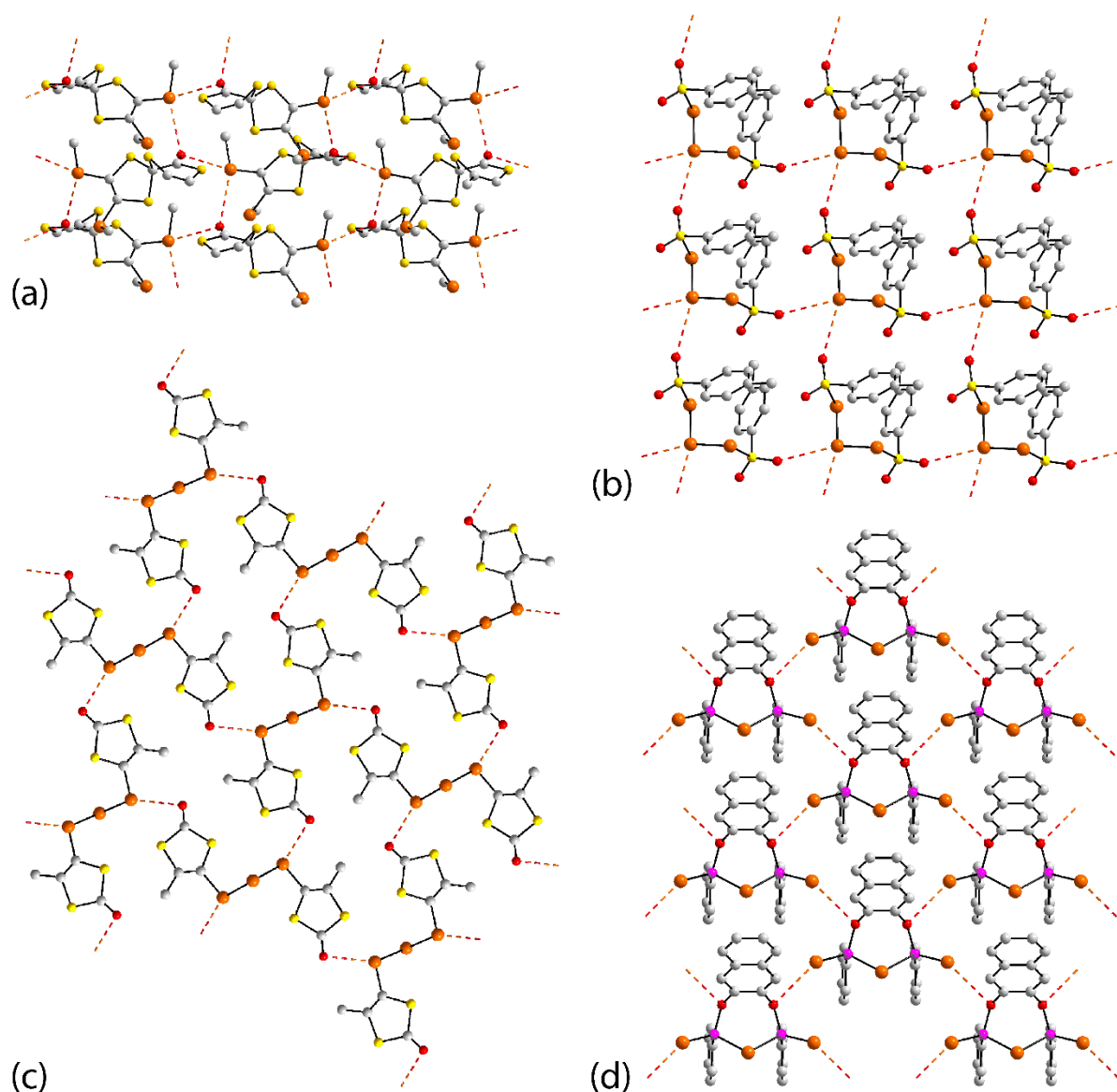
## 5.1 Two-dimensional assemblies formed by selenium(II) compounds

Several different motifs are noted in the two-dimensional arrays formed by the compounds in this section. In the crystal of mono-nuclear **181** [218], Fig. 18a, molecules assemble about a centre of inversion, being connected by  $\text{Se}\cdots\text{O}(\text{nitro})$  interactions and eight-membered  $\{\cdots\text{Se}\cdots\text{ONO}\}_2$  synthons. The connections extend laterally as each selenium forms two contacts as does each nitro group, via both oxygen atoms, with the resultant layer being corrugated. The selenium atom also forms two contacts in **182** [219] but, with the same, bifurcated carbonyl-oxygen atom to sustain a flat, hexagonal-like grid, Fig. 18b. In the following structures, disparate  $\text{Se}\cdots\text{O}$  interactions sustain the resulting two-dimensional array. In **183** [220], the selenium atom forms two interactions with carbonyl- and hydroxyl-oxygen atoms, derived from symmetry related molecules, which are linked by a hydroxyl-O– $\text{H}\cdots\text{O}(\text{carbonyl})$  hydrogen bond. In **184** [133], the connections are of the type  $\text{Se}\cdots\text{O}(\text{carbonyl})$  and  $\text{Se}\cdots\text{O}(\text{nitro})$ , and analogous contacts are formed in **185** [221], Fig. 18c. The layers in each of **183–185** have a jagged topology. There are two bi-nuclear selenium(II) compounds adopting two-dimensional aggregation patterns. In the first of these, **186** [222], each selenium atom forms a single contact to a common carbonyl-oxygen atom, Fig. 18d, leading to a flat, hexagonal pattern akin to that for **182**, Fig. 18b. In a variation, in **187** [223], each selenium atom again forms a single contact but, two different carbonyl-oxygen atoms, Fig. 18e, leading to a corrugated topology. A polymorph of **187** exists, i.e. **132**, which adopts a linear, one-dimensional chain in its crystal, Fig. 13d, forming the same number of  $\text{Se}\cdots\text{O}(\text{carbonyl})$  interactions. The difference in aggregation patterns arise as in **132**, centrosymmetric, eight-membered  $\{\cdots\text{SeC}_2\text{O}\}_2$  synthons are formed whereas in **187**, the molecules assemble through more open, 16-membered  $\{\cdots\text{SeC}_2\text{O}\}_4$  synthons, Fig. 18e.



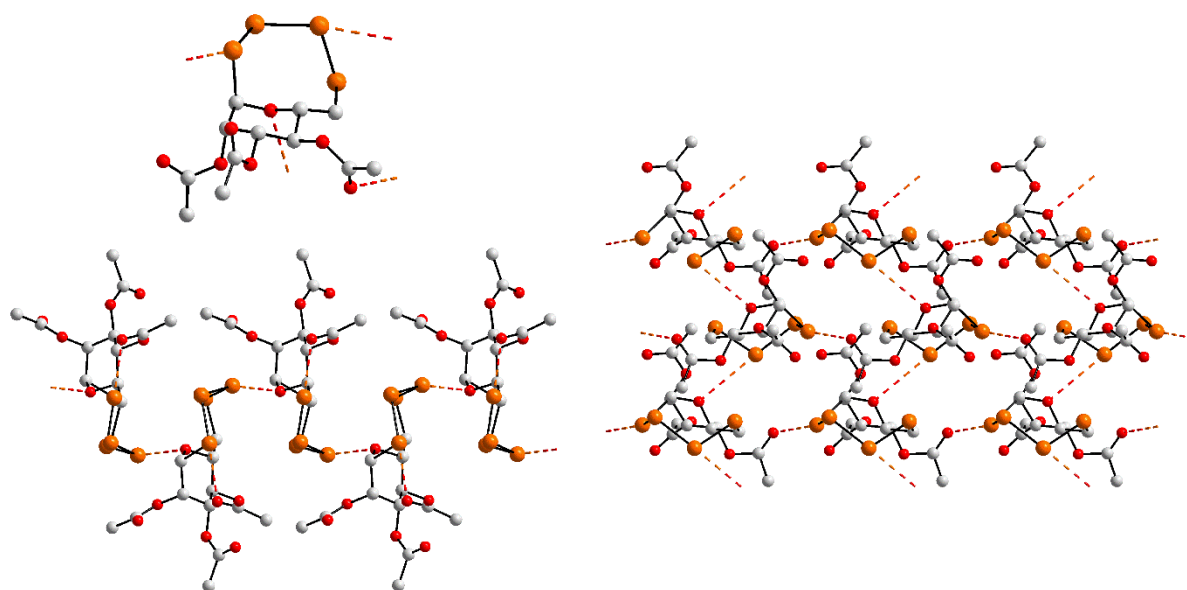
**Fig. 18.** Examples of supramolecular association in mono- and bi-nuclear selenium(II) compounds leading to two-dimensional arrays based on  $\text{Se}\cdots\text{O}$  chalcogen bonding interactions: (a) **181** [218;  $\text{Se}\cdots\text{O} = 3.01$  &  $3.17$  Å], (b) **182** [219;  $3.25$  Å], (c) **185** [221;  $3.06$  &  $3.16$  Å], (d) **186** [222;  $3.06$  &  $3.18$  Å] and (e) **187** [223;  $3.14$  Å].

Somewhat squarer arrangements are seen in the crystals of bi-nuclear **188** [224], Fig. 19a, where each molecule participates in four  $\text{Se}\cdots\text{O}(\text{carbonyl})$  interactions, with one of the selenium atoms forming two interactions and one of the carbonyl-oxygen atoms forming two interactions; the layer is corrugated. An even more square appearance is seen for **189** [186], Fig. 19b, where the central atom of the tri-nuclear molecule participates in two  $\text{Se}\cdots\text{O}(\text{sulphoxide})$  interactions with two different molecules while at the same time donating two sulphoxide-oxygen atoms to another two symmetry related molecules; the resultant layer is flat. In tri-nuclear **190** [225], which has two-fold symmetry with the central selenium atom lying on the axis, it is the external selenium atoms of the  $\text{Se}_3$  chain that each form a single  $\text{Se}\cdots\text{O}(\text{carbonyl})$  interaction and each of the carbonyl-oxygen atoms also participate in a  $\text{Se}\cdots\text{O}$  contact, Fig. 19c, leading to a corrugated layer. In tri-nuclear **191** [226], which has mirror symmetry with the central selenium lying on the plane, the selenide atoms lie to the periphery of the  $\text{Se}=\text{P}-\text{Se}-\text{P}=\text{Se}$  hetero-chain. In this instance, the selenide atoms form  $\text{Se}\cdots\text{O}(\text{phenoxide})$  contacts that generate a grid with a flat topology, Fig. 19d.



**Fig. 19.** Examples of supramolecular association in selenium(II) compounds leading to two-dimensional arrays based on  $\text{Se}\cdots\text{O}$  chalcogen bonding interactions: (a) **188** [224;  $\text{Se}\cdots\text{O} = 3.29$  &  $3.41$  Å], (b) **189** [186;  $3.22$  Å], (c) **190** [225;  $3.17$  Å] and (d) **191** [226;  $3.33$  Å].

The final selenium(II) compound adopting a two-dimensional array in its crystal is also the only example of a tetra-nuclear compound in this category, **192** [205]. Here, the four selenium atoms are in a  $\text{Se}_4$  chain and, as seen from Fig. 20, it is the 1,3-selenium atoms forming the  $\text{Se}\cdots\text{O}(\text{carbonyl})$  interactions with two different carbonyl-atoms that are responsible for the formation of the layer, which has a distinctive saw-tooth topology.

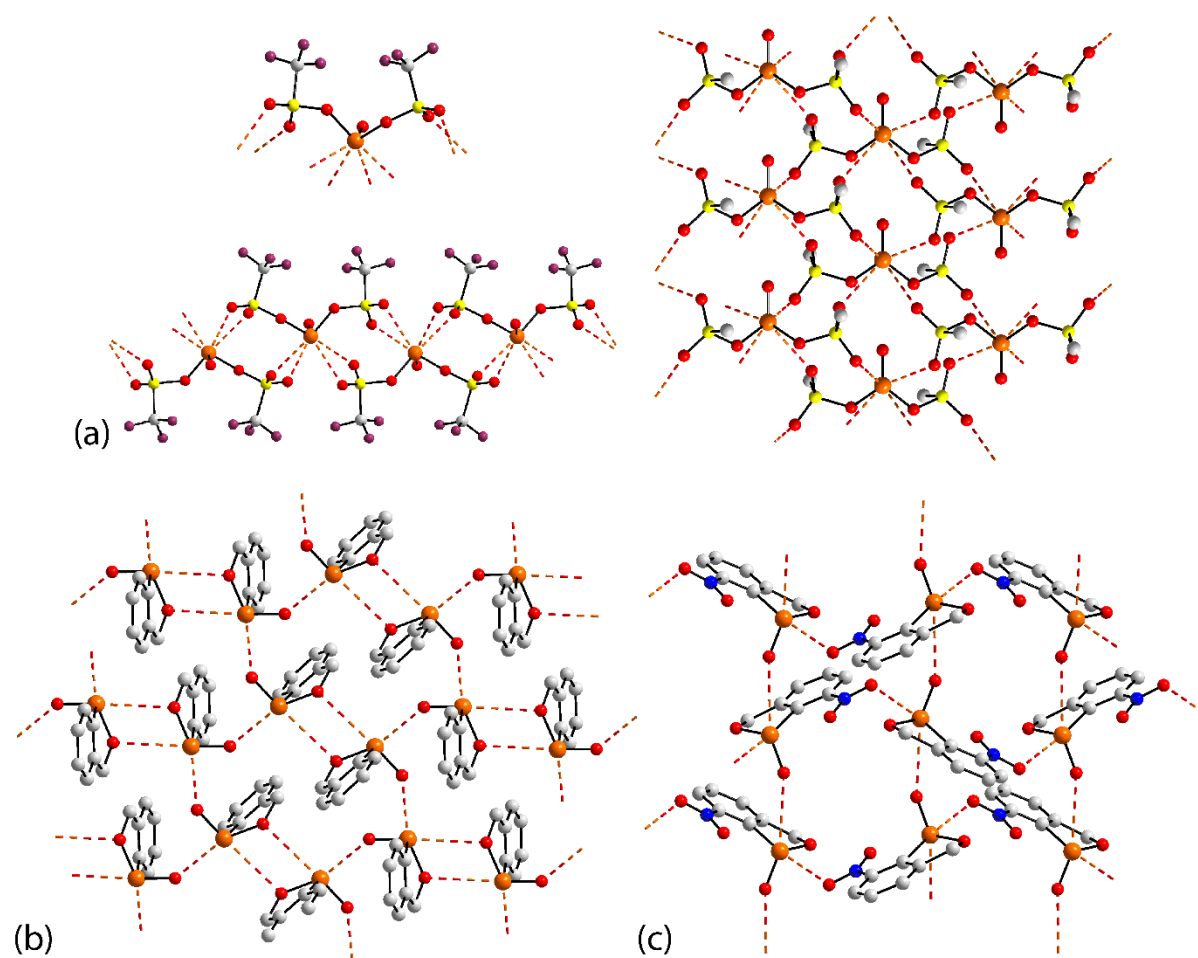


**Fig. 20.** Supramolecular association in **192** [205;  $\text{Se}\cdots\text{O} = 3.34 \text{ \AA} \text{ \& } 3.42 \text{ \AA}$ ], leading to two-dimensional arrays based on  $\text{Se}\cdots\text{O}$  chalcogen bonding: detail of the  $\text{Se}\cdots\text{O}(\text{carbonyl})$  interactions as well as a plan and a side-on view of the layer.

## 5.2 Two-dimensional assemblies formed by selenium(IV) compounds

A smaller number of selenium(IV) compounds assemble into two-dimensional arrays. The structure of **193** [227] is the only example in this series where the selenium atom is not incorporated within a ring. This open arrangement coupled with the selenium atom is within an  $\text{O}_3$ -donor set enables the formation of three interactions with each of the coordinated triflate anions, two of which are  $\text{Se}-\text{O}$  covalent bonds; each of the non-coordinating oxygen atoms participates in a  $\text{Se}\cdots\text{O}(\text{sulphonate})$  interaction, as seen from the detail of the selenium-atom environment of Fig. 21a. The packing comprises inter-digitated rows of molecules connected by the aforementioned  $\text{Se}\cdots\text{O}(\text{sulphonate})$  interactions to form a flat layer. In **194** [228], molecules are connected into centrosymmetric dimers via  $\text{Se}\cdots\text{O}(\text{phenoxide})$  interactions and these in turn are connected into a grid by  $\text{Se}\cdots\text{O}(\text{oxide})$  interactions which form the shorter of the separations, Fig. 21b. Disparate  $\text{Se}\cdots\text{O}$  interactions are evident in **195** [95] and **196** [113].

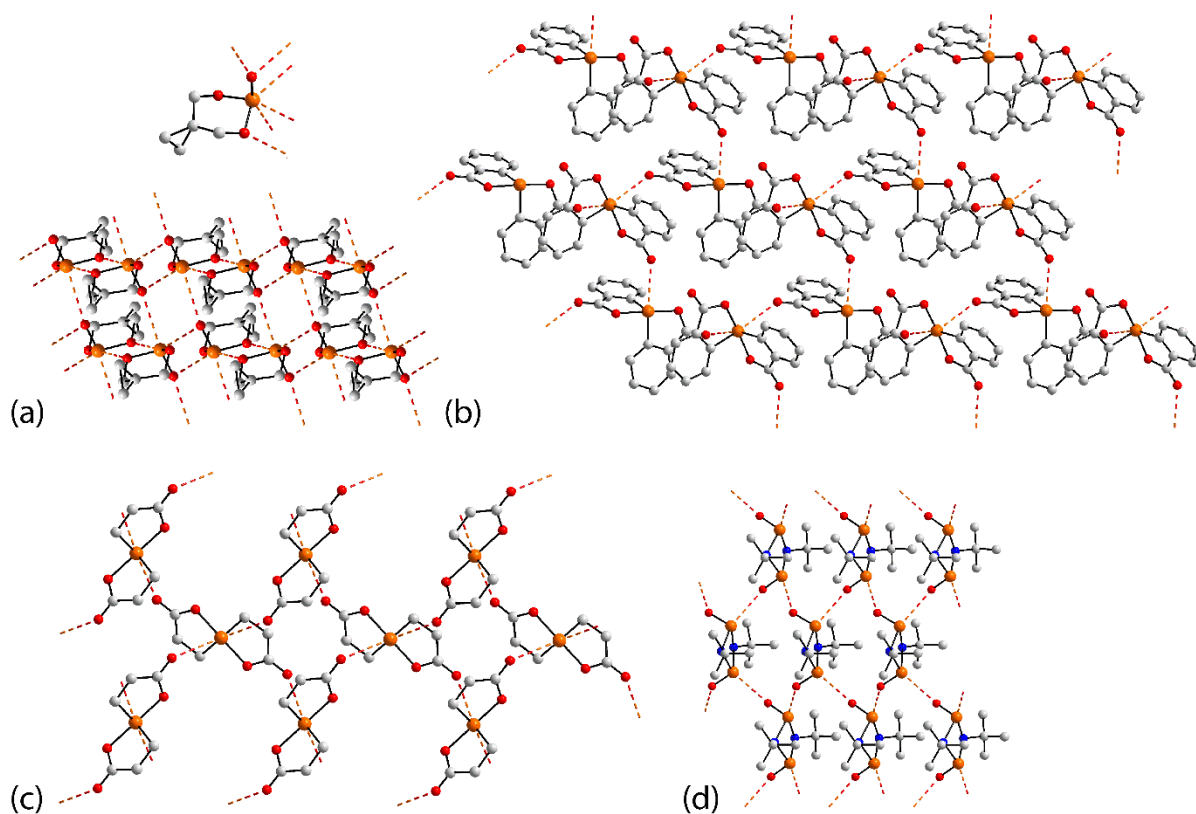
In the former, approximately orthogonal chains sustained by  $\text{Se}\cdots\text{O}(\text{nitro})$  and  $\text{Se}\cdots\text{O}(\text{oxide})$  interactions assemble molecules into a two-dimensional array, Fig. 21c. In **196**,  $\text{Se}\cdots\text{O}(\text{alkoxide})$  and  $\text{Se}\cdots\text{O}(\text{oxide})$  interactions cooperate in a similar fashion. The resultant layer in each of **195** and **196** is jagged.



**Fig. 21.** Examples of supramolecular association in selenium(IV) compounds leading to two-dimensional arrays based on  $\text{Se}\cdots\text{O}$  chalcogen bonding interactions: (a) **193** [227;  $\text{Se}\cdots\text{O} = 2.76, 2.91, 3.14 \text{ \AA}$ ] showing detail of the  $\text{Se}\cdots\text{O}(\text{sulphoxide})$  interactions as well as a plan (fluoride atoms omitted) and a side-on view of the layer, (b) **194** [228;  $2.76 \text{ \AA}$  &  $3.29 \text{ \AA}$ ] and (c) **195** [95;  $3.13 \text{ \AA}$  &  $3.26 \text{ \AA}$ ].

The selenium atom in **197** [133] is incorporated within a six-membered ring and forms a total of three Se $\cdots$ O interactions in the crystal, Fig. 22a. Centrosymmetrically related molecules are connected by via Se $\cdots$ O(alkoxide) interactions, forming the shorter distances, and these are connected into a flat, two-dimensional array by Se $\cdots$ O(oxide) interactions. Two independent molecules comprise the asymmetric unit of **198** [229] and these are connected by Se $\cdots$ O(carbonyl) interactions to form the array shown in Fig. 22b; the topology of the layer is flat. The selenium atom in the first independent molecule forms two Se $\cdots$ O contacts and the carbonyl-O atom one, with the second independent molecule following the opposite trend. This flexibility in association via Se $\cdots$ O contacts is reflected in the following observation. Compound **198** is of particular interest as three polymorphs have been reported. Earlier in this survey, aggregation patterns were reported for the first two of these, i.e. **172** and **173**, Fig. 16h, each of which adopts a zig-zag chain in their crystal sustained, on average, by one and two Se $\cdots$ O(carbonyl) interactions, respectively. The selenium atom in **199** [230] is bis-chelated by C,O-donors and lies on a two-fold axis of symmetry. The selenium atom forms two Se $\cdots$ O(contacts) to form a flat, two-dimensional array, Fig. 22c. The only bi-nuclear compound in this section is found in **200** [231] where diagonally opposite selenium atoms are incorporated within a four-membered ring; the molecule has mirror symmetry with the nitrogen atoms of N<sub>2</sub>Se<sub>2</sub> core lying on the plane. Each of the selenium and carbonyl-oxygen atoms forms a single Se $\cdots$ O(carbonyl) contact extending laterally to form a corrugated layer, Fig. 22d.

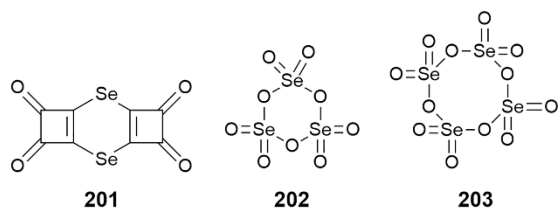




**Fig. 22.** Examples of supramolecular association in selenium(IV) compounds leading to two-dimensional arrays based on Se...O chalcogen bonding interactions: (a) **197** [113; Se...O = 2.82, 3.13 & 3.18 Å] showing detail of the Se...O interactions as well as a plan view of the layer, (b) **198** [229; 2.96, 2.97 & 3.16 Å], (c) **199** [230; 3.09 Å] and (d) **200** [231; 3.06 Å].

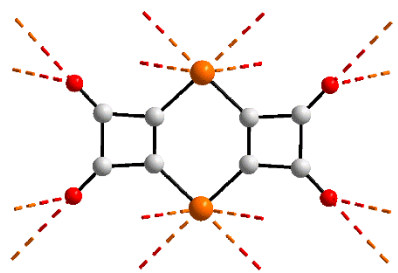
## 6. Three-dimensional assemblies mediated by Se...O chalcogen bonding

There are only three examples of selenium compounds comprising one chemical entity in the crystal assembling into a three-dimensional architecture based on Se...O chalcogen bonding. The chemical structures for these oxide-rich molecules, i.e. **201–203** [118, 232], are shown in Fig. 23.

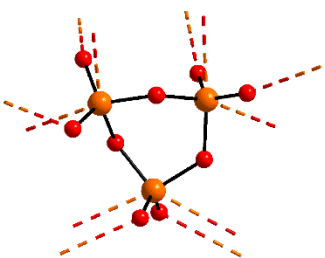
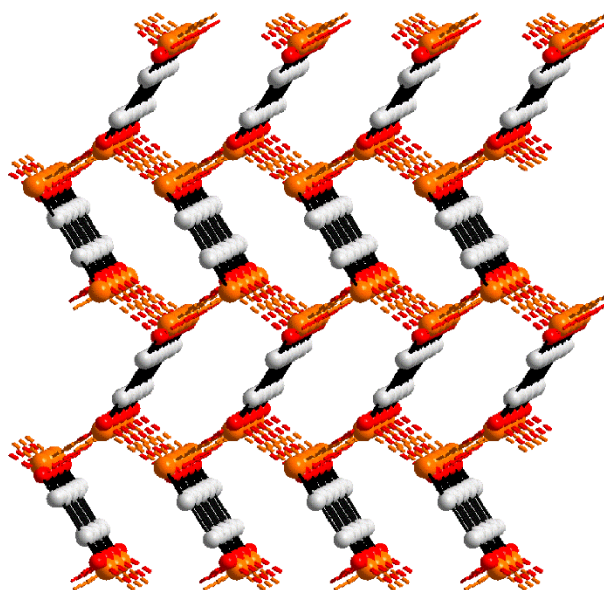


**Fig. 23.** Chemical diagrams for the interacting species, **201–203**, in selenium(II) and selenium(VI) compounds featuring  $\text{Se}\cdots\text{O}$  contacts leading to supramolecular, three-dimensional arrays.

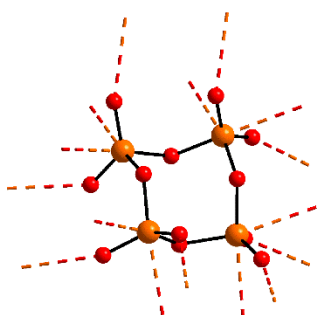
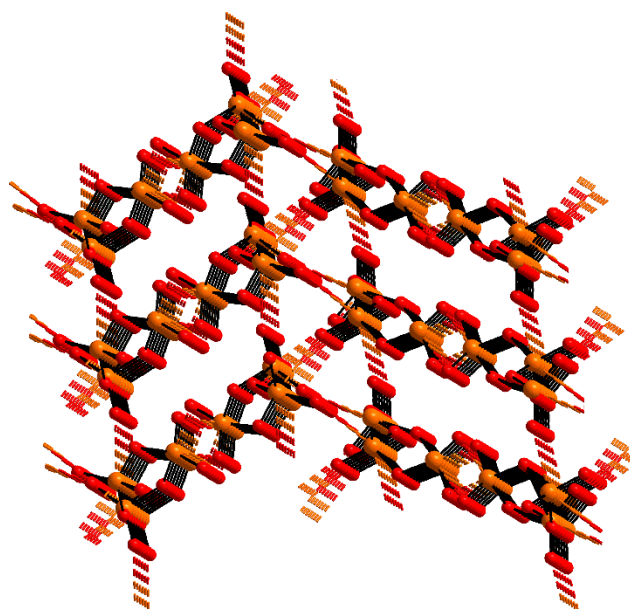
Only one selenium(II) molecule assembles to form a three-dimensional architecture in its crystal, namely **201** [232]. The bi-nuclear molecule has mirror symmetry containing both selenium atoms and relating the two cyclobutadiene residues. Here, each selenium atom forms four  $\text{Se}\cdots\text{O}(\text{carbonyl})$  interactions and each of the carbonyl-oxygen atoms forms two interactions to selenium as highlighted in Fig. 24a. The resulting architecture resembles a skewed honeycomb array. The two remaining molecules feature selenium(VI) centres, i.e. tri-nuclear **202** [118] and tetra-nuclear **203** [118]. In the former, which lacks symmetry, only the oxide-oxygen atoms participate in  $\text{Se}\cdots\text{O}$  interactions with each forming a single contact and each selenium atom forming two  $\text{Se}\cdots\text{O}(\text{oxide})$  contacts, Fig. 24b. Layers with a zig-zag topology are discernible in the packing, Fig. 24b, being connected by three distinct  $\text{Se}\cdots\text{O}(\text{oxide})$  contacts. The molecule in **204** is disposed about a four-fold centre of inversion ( $\bar{4}$ ) with each  $\text{Se}(=\text{O})_2$  unit involved in two donor and two acceptor  $\text{Se}\cdots\text{O}(\text{oxide})$  contacts, Fig. 24c. The resulting architecture comprises tetra-nuclear molecules assembled into columns, with a square appearance, connected orthogonally by the  $\text{Se}\cdots\text{O}(\text{oxide})$  contacts which define columns with a rectangular appearance, Fig. 24c.



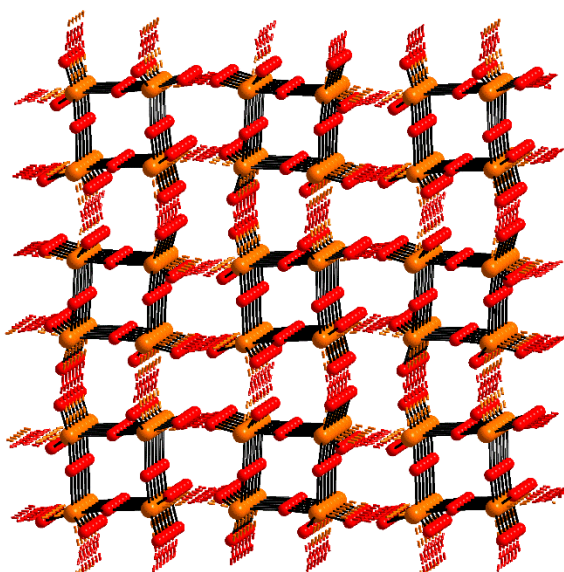
(a)



(b)



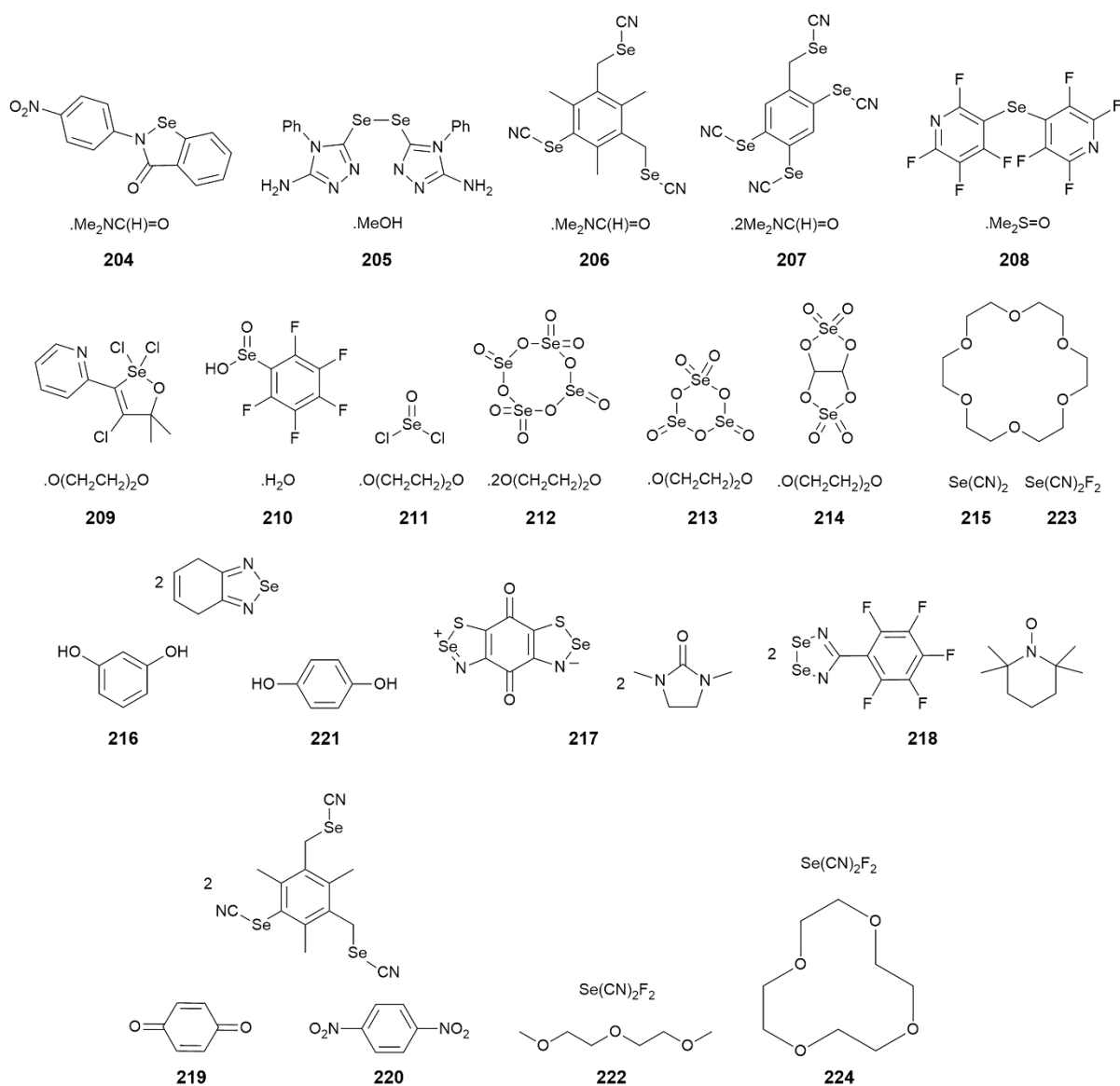
(c)



**Fig. 24.** Supramolecular association in selenium(II) and selenium(VI) compounds leading to three-dimensional arrays based on Se $\cdots$ O chalcogen bonding interactions showing detail of the Se $\cdots$ O interactions as well as a perspective of the three-dimensional assembly: (a) **201** [232; Se $\cdots$ O = 3.19 & 3.39 Å], (b) **202** [118; 3.03-3.33 Å] and (c) **203** [118; 3.13 & 3.15 Å].

## **7. Supramolecular assemblies of multi-component species mediated by Se $\cdots$ O chalcogen bonding**

For completeness, in this section Se $\cdots$ O chalcogen bonding interactions in multi-component crystals are surveyed. Firstly, solvates are described followed by co-crystals. The chemical structures of the 20 compounds covered in this section, **204–224** [118, 233-245] are shown in Fig. 25.



**Fig. 25.** Chemical diagrams for the interacting species, **204–224**, in selenium(II) and selenium(IV) compounds featuring  $\text{Se}\cdots\text{O}$  contacts leading to supramolecular, two-dimensional arrays.

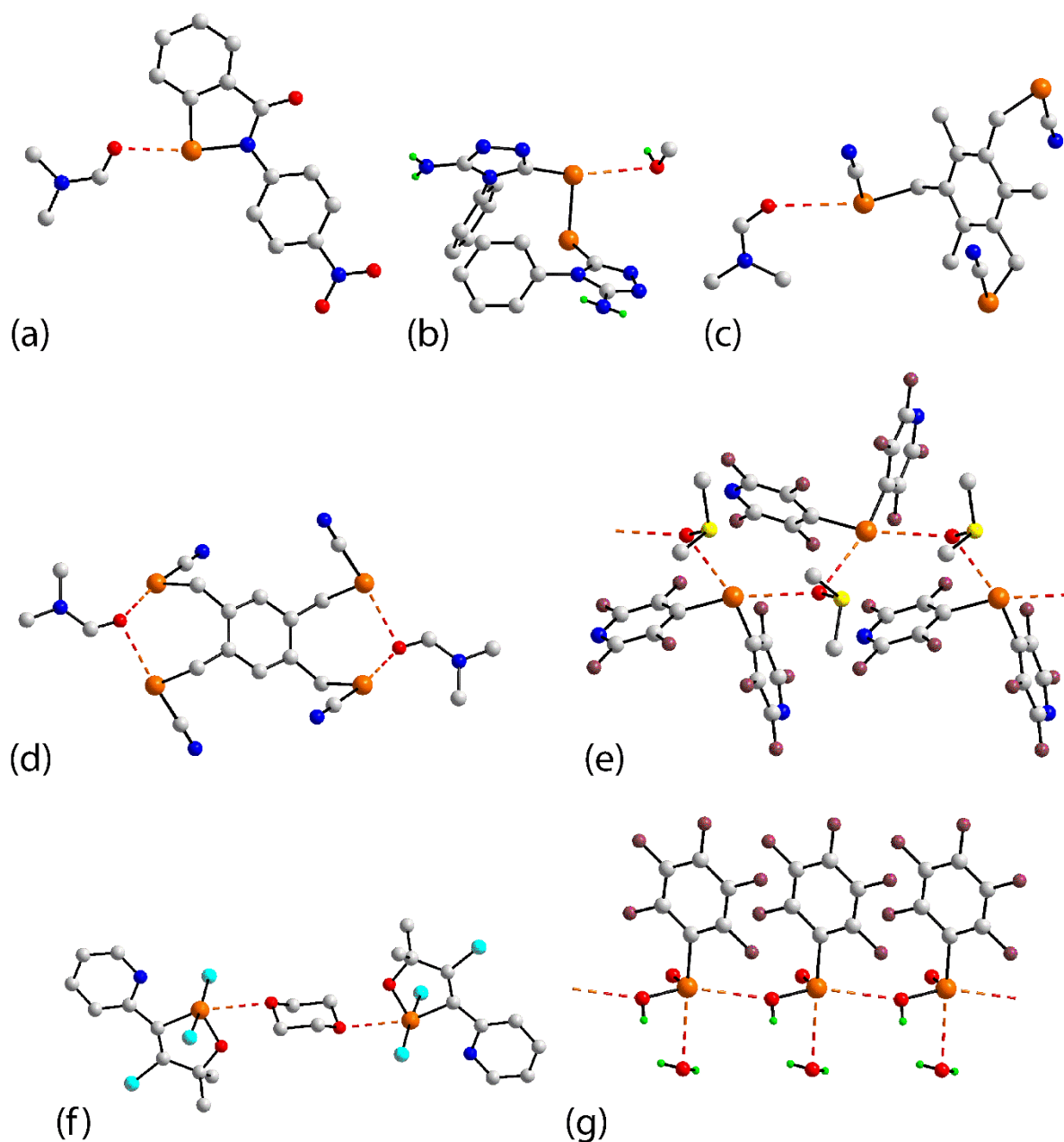
## 7.1 Supramolecular assemblies in solvates of selenium compounds

Each of the mono-, bi- and tri-nuclear selenium(II) compounds, i.e. **204** [233], **205** [234] and **206** [235], illustrated in Figs 26a-c, respectively, feature a single  $\text{Se}\cdots\text{O}$  contact between the molecule and solvent, i.e. dimethylformamide in **204** and **206**, and methanol in **205**. In tetra-nuclear **207** [236], which is disposed about a centre of inversion, there are two

co-crystallised dimethylformamide molecules and the oxygen atom from each of these symmetrically spans two selenium atoms to form a three-molecule aggregate shown in Fig. 26d.

A one-dimensional chain with a zig-zag topology (glide symmetry) is formed in the crystal of **208** [236] whereby the dimethylsulphoxide-oxygen atom symmetrically bridges two selenium atoms to form the arrangement shown in Fig. 26e.

The focus now turns towards selenium(IV) species. A three-molecule aggregate is formed in **209** [237] where the dioxane molecule, situated about a centre of inversion, bridges two molecules as shown in Fig. 26f. A hydrated, linear supramolecular chain is formed in the crystal of **210** [238]. The water molecule is connected to the selenium atom, being separated by 2.92 Å, and the resultant two molecule aggregates assemble into a chain via  $\text{Se}\cdots\text{O}(\text{hydroxyl})$  chalcogen bonds (3.03 Å) as shown in Fig. 26g.



**Fig. 26.** Supramolecular association in selenium(II) and selenium(IV) compounds leading to zero- and one-dimensional assemblies based on  $\text{Se}\cdots\text{O}$  chalcogen bonding interactions: (a) **204** [233;  $\text{Se}\cdots\text{O} = 2.64 \text{ \AA}$ ], (b) **205** [234;  $3.06 \text{ \AA}$ ], (c) **206** [235;  $3.28 \text{ \AA}$ ], (d) **207** [235;  $2.94$  &  $2.95 \text{ \AA}$ ], (e) **208** [236;  $2.89$  &  $2.90 \text{ \AA}$ ], (f) **209** [237;  $2.83 \text{ \AA}$ ] and (g) **210** [238;  $2.92$  &  $3.03 \text{ \AA}$ ].

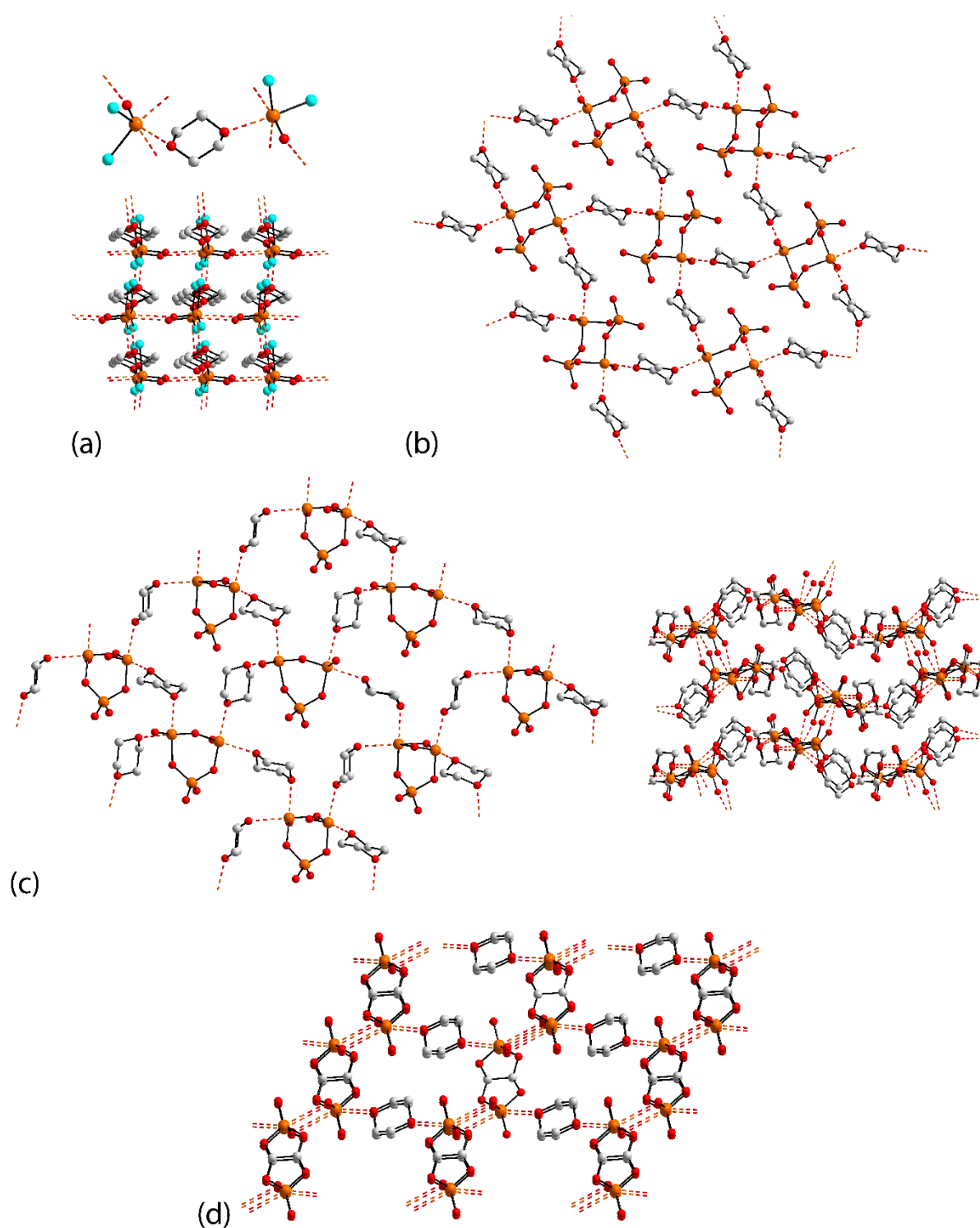
In the mono-selenium(IV) compound **211** [239], linear chains are sustained by  $\text{Se}\cdots\text{O}(\text{oxide})$  contacts and these are connected into a three-dimensional array by links provided

by bridging dioxane molecules, Fig. 27a. Thus, each selenium forms three  $\text{Se}\cdots\text{O}$  interaction with the shorter of the separations involving  $\text{Se}\cdots\text{O}(\text{ether})$  contacts.

There are two mixed selenium(IV)/(VI) compounds in this category, i.e. **212** [118] and **213** [118], and a pivotal role for the co-crystallised dioxane molecules is evident in each. The tetra-nuclear molecule in **212** is disposed about a centre of inversion. There are two molecules of solvent for each tetra-nuclear molecule and it is the selenium(IV) centres that associate with two symmetry dioxane molecules to form a two-dimensional grid, Fig. 27b. In the second mixed valence compound, **213** [118], two tri-nuclear molecules and four dioxane molecules comprise the asymmetric unit. As shown in the left-hand image of Fig. 27c, molecules are assembled into a two-dimensional array with an undulating topology via  $\text{Se}\cdots\text{O}(\text{ether})$  interactions as each dioxane molecule is bridging and each selenium(IV) centre forms two contacts of this type. The links between layers to form a three-dimensional architecture are of the type  $\text{Se}\cdots\text{O}(\text{oxide})$ , where the oxide-donors are bounds to the selenium(VI) centres. The  $\text{Se}\cdots\text{O}(\text{oxide})$  interactions form separations systematically longer than the  $\text{Se}\cdots\text{O}(\text{ether})$  contacts.

A three-dimensional architecture is also found in the crystals of the selenium(VI) compound, **214** [118], a 1:1 dioxane solvate, with the bi-nuclear molecule bisected by two-fold axis of symmetry and with the dioxane molecule disposed about a centre of inversion. As seen in Fig. 24d, molecules are assembled into rows via  $\text{Se}\cdots\text{O}(\text{oxide})$  interactions and rows are connected by  $\text{Se}\cdots\text{O}(\text{ether})$  interactions derived from the bridging dioxane molecules. A systematic trend is noted in  $\text{Se}\cdots\text{O}$  distances as for **213** in that the separations involving the  $\text{Se}\cdots\text{O}(\text{ether})$  contacts are shorter than the  $\text{Se}\cdots\text{O}(\text{oxide})$  contacts.

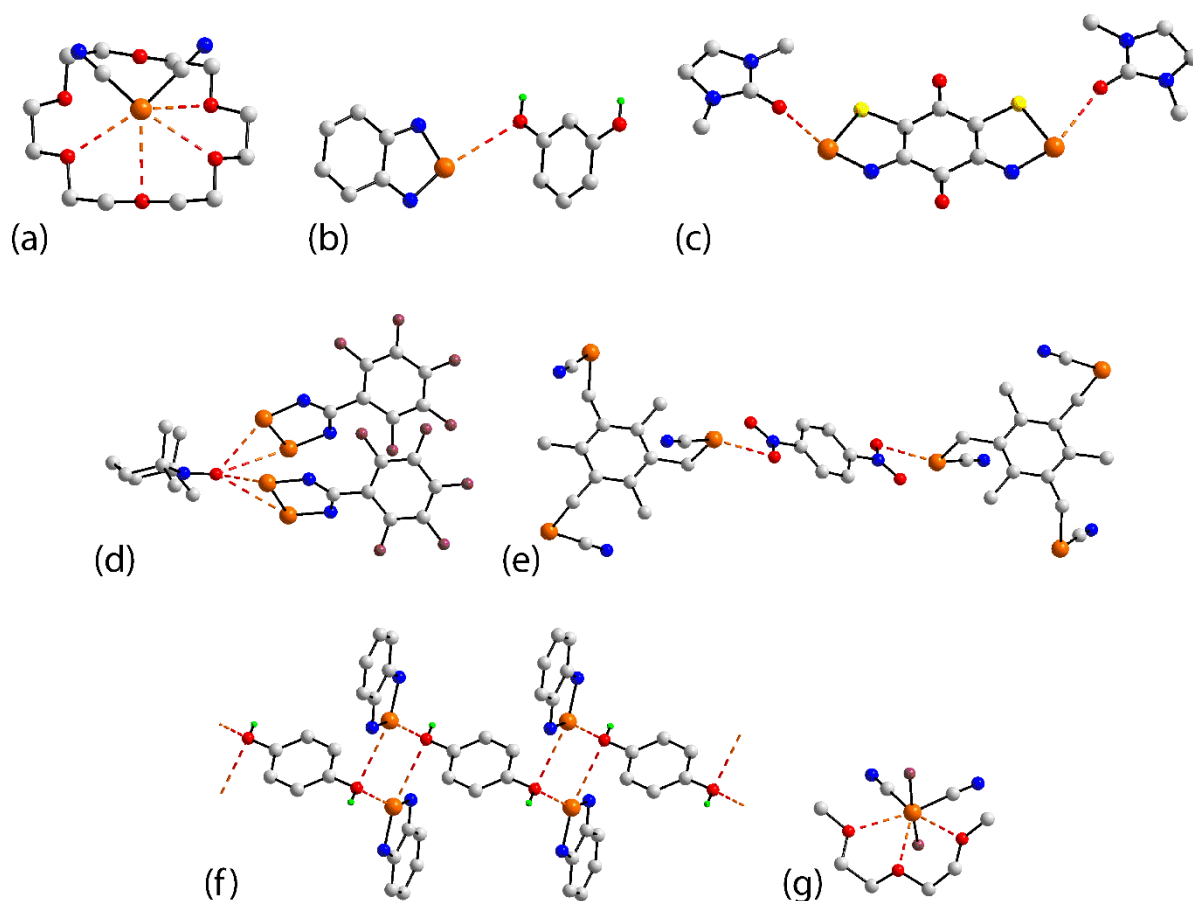




**Fig. 27.** Supramolecular association in selenium(IV), mixed selenium(IV)/(VI) and selenium(VI) compounds leading to two- and three-dimensional assemblies based on Se...O chalcogen bonding interactions: (a) **211** [239; Se...O = 2.61, 2.72 & 2.90 Å], (b) **212** [118; 2.40 & 2.44 Å], (c) **213** [118; Se...O(ether) 2.44-2.62 Å and Se...O(oxide) 2.82 & 3.07 Å] and (d) **214** [118; 2.83 & 3.13 Å].

## 7.2 Supramolecular assemblies in selenium(II) co-crystals

In this final section, a number of selenium(II) and selenium(IV) aggregates are described, with all but one example being zero-dimensional in consideration of  $\text{Se}\cdots\text{O}$  interactions alone. The selenium(II) atom in mono-nuclear **215** [240] forms four  $\text{Se}\cdots\text{O}(\text{ether})$  contacts to sustain a two-molecule aggregate, Fig. 28a. The asymmetric unit of **216** [241] comprises two selenium(II) molecules and the organic co-former, i.e. is a 2:1 co-crystal, one of the selenium(II) molecules makes a single  $\text{Se}\cdots\text{O}(\text{hydroxyl})$  interaction to form the two-molecule aggregate shown in Fig. 28b. In the 1:2 co-crystal **217** [242], each of the selenium atoms in the bi-nuclear molecule forms a  $\text{Se}\cdots\text{O}(\text{carbonyl})$  interaction to form a three-molecule aggregate, Fig. 28c. Another bi-nuclear molecule where the selenium atoms are connected to each other within a five-membered ring, **218** [243], forms a 2:1 co-crystal with a nitrogen-oxo-containing molecule; both species are radicals. The oxo atoms atom accepts four  $\text{Se}\cdots\text{O}(\text{oxo})$  interactions, one each from each of the selenium atoms of the two co-formers, Fig. 28d. The tri-nuclear molecules in each of **219** and **220** [244] featured earlier in **206**, i.e. forming a two-molecule aggregate with a solvent molecule, Fig. 26c. In **219** and **220**, Fig. 28e, this molecule is also a co-former in 2:1 co-crystals with potentially bridging molecules, at least via  $\text{Se}\cdots\text{O}$  interactions; the organic co-former is disposed about a centre of inversion in both co-crystals. Indeed, one selenium(II) atom in each molecule is connected by  $\text{Se}\cdots\text{O}(\text{carbonyl})$  and  $\text{Se}\cdots\text{O}(\text{nitro})$  interactions in **219** and **220**, respectively, to form a three-molecule aggregate in each case.



**Fig. 28.** Supramolecular association in selenium(II) and selenium(IV) co-crystals leading to zero- and one-dimensional assemblies based on  $\text{Se}\cdots\text{O}$  chalcogen bonding interactions: (a) **215** [240;  $\text{Se}\cdots\text{O} = 2.87\text{--}3.40\text{ \AA}$ ], (b) **216** [241;  $3.18\text{ \AA}$ ], (c) **217** [242;  $2.83\text{ \AA}$ ], (d) **218** [243;  $2.90\text{--}3.35\text{ \AA}$ ], (e) **220** [244;  $3.23\text{ \AA}$ ], (f) **221** [241;  $3.14\text{ \& } 3.28\text{ \AA}$ ] and (g) **222** [240;  $2.66\text{--}2.85\text{ \AA}$ ].

The only one-dimensional chain in this section is formed in the 2:1 co-crystal **221** [241]; the selenium(II) molecule also formed a solvate via a  $\text{Se}\cdots\text{O}(\text{hydroxyl})$  interaction in **216** [241], Fig. 28b. In **221**, the benzene-1,4-diol molecule is situated about a centre of inversion and the association between molecules is also through  $\text{Se}\cdots\text{O}(\text{hydroxyl})$  interactions. Centrosymmetric  $\{\cdots\text{Se}\text{--O}\}_2$  synthons are formed in the crystal leading to a linear, supramolecular chain, Fig. 28f.

### 7.3 Supramolecular assemblies in selenium(IV) co-crystals

There are four selenium(IV) molecules forming co-crystals based on  $\text{Se}\cdots\text{O}$  chalcogen bonding, i.e. **222**, **223** and **224** [240]. In **222**, Fig. 28g, the selenium(IV) atom forms three  $\text{Se}\cdots\text{O}(\text{ether})$  contacts to form a zero-dimensional adduct. Similar, two molecule aggregates are formed in **223** and **224** where each selenium atom forms four  $\text{Se}\cdots\text{O}(\text{ether})$  contacts, resembling the situation illustrated for **215** [240] in Fig. 28a.

## 8. Overview

Allowing for multiple molecules in the asymmetric unit and the occurrence of several polymorphs, 224 distinct supramolecular aggregation patterns based on  $\text{Se}\cdots\text{O}$  chalcogen bonding interaction are noted in the crystals of nearly 220 selenium compounds. The overwhelming majority of the compounds were homogeneous but examples of solvate and co-crystals are evident. By far the most predominant oxidation state is +II, with 163 examples (72%), followed by +IV (51) with a small number of compounds with selenium in the +VI (8) oxidation state; two mixed valent selenium(IV)/(VI) compounds are also included in the survey. Over two-thirds of molecules are mono-nuclear (161), with decreasing numbers of bi-, tri- and tetra-molecules, i.e. 43, 11 and nine, respectively. A full range of zero-, one-, two- and three-dimensional patterns are noted with the majority, i.e. over 55% (128 examples), being one-dimensional with the next most significant being, zero-dimensional, with 69 examples. There are 22 examples of molecules assembled into two-dimensional arrays and five forming three-dimensional architectures. The average number of  $\text{Se}\cdots\text{O}$  interactions per participating species varies from 0.5, i.e. for zero-dimensional aggregates sustained by a single interaction to four in several architectures. Of the nearly 300 different  $\text{Se}\cdots\text{O}$  contacts in the supramolecular aggregates described herein, over three-quarters (78%) involve a single  $\text{Se}\cdots\text{O}$  interaction and 18% involve two  $\text{Se}\cdots\text{O}$  interactions. There are six examples each of molecules

where the selenium forms three or four contacts, always in higher-dimensional aggregates. Of the zero-dimensional aggregates, the majority comprise two like-molecules sustained by one (9) or two (41)  $\text{Se}\cdots\text{O}$  interactions but, examples of four- and six-molecule aggregates are also observed. A variety of topologies are noted among the 125 zero-dimensional chains, including linear (38), zig-zag (52), helical (30) and twisted (5).

The large range of supramolecular aggregation patterns is complimented by the diversity in the oxygen donors participating in  $\text{Se}\cdots\text{O}$  interactions. When aggregates featuring one type of  $\text{Se}\cdots\text{O}$  interaction only, 41% involve carbonyl donors. The next most prevalent are ether (including methoxy) and  $\text{Se}=\text{O}$  donors, each at 12%, followed by nitro-, sulphoxide- and hydroxyl-donors at 9, 8 and 6%, respectively.

Attention is now directed on the propensity of molecules to form  $\text{Se}\cdots\text{O}$  chalcogen bonding in their crystals. Herein, 224 examples of aggregates sustained by  $\text{Se}\cdots\text{O}$  chalcogen bonding interactions were identified. Put into perspective, after a search of the CSD [65] following the protocols outlined in section 2, there are 1722 “hits” for crystals containing both selenium and oxygen. This implies the percentage adoption of  $\text{Se}\cdots\text{O}$  chalcogen bonding approximates 13% of all possible structures where these interactions can occur. This percentage is an underestimate as in the present survey as crystals where  $\text{Se}\cdots\text{O}$  interactions were acting in concert with other identifiable intermolecular forces, the notable example being hydrogen bonding, were omitted. This percentage compares favourably to the 6% of selenium(lone-pair) $\cdots\pi$ (arene) interactions in crystals where these interactions can potentially form [248,249]. Over and above different chemical composition, as alluded to above, secondary bonding interactions, including chalcogen bonding interactions, are notoriously subject to steric effects in that these interactions are mitigated when bulky metal-bound and/or ligand-bound substituents are present [54, 56-63]. To probe further the likely adoption of

Se $\cdots$ O interactions in crystals, the likelihood of specific classes of compounds to form Se $\cdots$ O chalcogen bonds was ascertained.

As noted above, Se $\cdots$ O(carbonyl) interactions featured in 41% of the crystals in the present survey. Hence, the CSD was searched for “selenium” and “carbonyl-oxygen” using the established protocols. This indicated that almost 50% of all crystals having these two components actually formed Se $\cdots$ O(carbonyl) interactions. An analogous search for residues containing Se=O, often observed in the selenium(IV) compounds included herein, was conducted. This analysis indicated a smaller percentage adoption of about 25%. Throughout this survey, the 5-selanylidene-1H-pyrrol-2-one core, as found in Ebselen<sup>TM</sup>, has been mentioned a good number of times. This core has a three-bond separation between the selenium and carbonyl-oxygen atoms, and with these acceptor and donor atoms largely constrained to a fixed disposition owing to their relationship through the five-membered ring. A search of the CSD revealed this core features in 52 crystals. With Se $\cdots$ O(carbonyl) interactions forming in 25 examples, the percentage adoption is over 48%. Interestingly, five others of these structures formed Se $\cdots$ O interactions in their crystals but, with selenide- (1), nitro- (1) and hydroxyl-oxygen (3) donors. With this relatively high adoption rate, the propensity of selenium molecules with selenium incorporated within a five-membered ring comprising four unspecified atoms and unspecified bonds between them was then evaluated. The CSD has about 945 “hits” for this fragment and with 102 examples having unassisted Se $\cdots$ O chalcogen bonding interactions, the percentage adoption is at least 10%, indicating this fragment alone does not promote Se $\cdots$ O interactions.

Consideration is now directed towards the geometric parameters characterising the observed Se $\cdots$ O secondary bonding interactions. The Se $\cdots$ O separations span a wide range, i.e. from a short 2.40 Å, indicative of some covalent character, right out to the van der Waals limit of 3.42 Å; the average distance of a Se $\cdots$ O interaction computes to 3.11 Å and the median value

is 3.17 Å. It is noted that while many of the shorter interactions were in the dioxane adducts, such as **212** which exhibited the short contact cited above, short contacts were often noted in one-dimensional chains involving molecules incorporating the 5-selanylidene-1H-pyrrol-2-one core, e.g. the next shortest separation of 2.41 Å is observed in **118**. However, these are only generalisations, with each class of molecule, respectively, also having longer contacts, e.g. 3.35 Å in **8** and 3.38 Å in **23**. This observation is entirely consistent with the well-known axiom in supramolecular chemistry that geometric correlations of weak intermolecular interactions are not generally possible unless the molecules/interactions are very closely related/isostructural [245-247]. In the present case, the lack of systematic trends is not surprising considering the different chemical composition of the interacting species, different oxidation states and geometries, and range of oxygen donors engaged in the Se $\cdots$ O interactions.

Up to this point, no specific mention of the angles associated with the supramolecular Se $\cdots$ O interactions has been made; key angles subtended at oxygen donor atoms and selenium acceptor atoms are collated in Appendix A. Just as distance correlations are not reliable for intermolecular interactions [245-247], correlations involving angles are also problematic, as commented upon recently for secondary bonding interactions formed between selenium and the heavier main group elements [250]. This is because, as for distances, angles are going to be moderated by the chemical/electronic environment of the participating atoms. Based on the assumption that for the specified Se $\cdots$ O contacts, the oxygen atom is the Lewis base, providing the charge to the  $\sigma$ -hole located on the selenium atom of the Lewis acid, there are several variables impacting upon the magnitude of the Se $\cdots$ O interaction and the angles subtended at the interacting oxygen atom. In the case of the oxygen donor, these factors include but, are not limited to the steric and electronic profiles of the residues bound to oxygen, the hybridisation of the oxygen atom and, when the interacting oxygen atom is part of a nitro group, the partial charge on the oxygen atom. For the selenium acceptor, again the steric and electronic profiles

of bound atoms/groups come into play, as does the ligand donor set about the selenium atom along with the oxidation state of the selenium atom which, in turn, impacts on the number of sterically active lone-pairs of electrons about the selenium atom and therefore, stereochemistry.

These points are highlighted in the following observations on the sub-set of structures where the donor oxygen and acceptor selenium atoms participate in one contact only. Considering the angles subtended at the oxygen donors first, in the surveyed structures featuring a single contact between the participating atoms, the minimum angle of  $82.4^\circ$  (the  $\text{Se}\cdots\text{O}$  separation is  $3.38\text{ \AA}$ ) was found in **105** where the donor atom is a carbonyl-O to a selenium(II) centre, and the maximum angle of  $160.2^\circ$  ( $\text{Se}\cdots\text{O} = 2.83\text{ \AA}$ ) is seen in **217** where a carbonyl-O atom is the donor and the acceptor is a selenium(II) atom flanked by nitrogen and sulphur atoms within a five-membered ring. The large range observed overall is also reflected in more specific contacts, for example  $\text{S}-\text{O}\cdots\text{Se}$  contacts with a range of over  $70^\circ$ , i.e. from  $87.7^\circ$  in **2** to  $159.7^\circ$  in **78** with a spread of values within this range for the 10 structures having the oxygen and selenium atoms forming a single contact only. The above notwithstanding, the following represents an analysis of specific types of  $\text{Se}\cdots\text{O}$  interactions.

For the  $\text{sp}^3$ -hybridised hydroxyl-O atom, there are 11 examples and the range of values is somewhat reduced compared to the general survey, i.e.  $94.1^\circ$  in **13** to  $126.2^\circ$  in **15** if an outlier, i.e. **3** ( $144.7^\circ$ ), is ignored. While, generally, these values are in the generally expected range for a  $\text{sp}^3$ -hybridised-O(lone-pair) $\cdots\sigma$ -hole(Se) interaction, the influence of hydrogen bonding interactions, for example, might also be expected to cause distortions, as in outlier **3**. Conversely, if selenium-bound lone-pair of electrons is anticipated in a position diagonally opposite to a covalent bond involving selenium and carbon (or nitrogen or phosphorus), a close to linear angle at selenium would be anticipated. In the present series of structures involving hydroxyl-donors, these angles range from  $148.6^\circ$  for  $\text{C}-\text{Se}\cdots\text{O}$  in **15**, where the selenium(II)



atom is part of five-membered ring to  $175.0^\circ$  for N–Se $\cdots$ O in **118**, where the selenium(II) atoms is flanked by carbon and nitrogen donors within a five-membered ring.

A number of structures are constructed about a  $\{\cdots\text{Se}=\text{O}\}_2$  core and present a robust set of Se=O $\cdots$ Se and A–Se $\cdots$ O angles, where A = C, N or S. Only two examples of selenium(II) feature this core, i.e. **25** and **26**, each resulting in a zero-dimensional aggregation, with pairs of Se=O $\cdots$ Se and A–Se $\cdots$ O angles of  $108.3$  and  $156.5^\circ$ , and  $111.2$  and  $156.1^\circ$ , respectively. For the 15 selenium(IV) species, the Se=O $\cdots$ Se angles range from  $88.0^\circ$ , for **43**, to  $121.4^\circ$  for **44**. In fact, these are outliers (see below) with the remaining angles lying between  $93.2^\circ$ , for **37**, to  $108.4^\circ$  for **42**. In terms of A–Se $\cdots$ O angles, these are consistently wider than for the selenium(II) species, lying between  $163.6^\circ$ , for **37** (A = C), to  $177.5^\circ$  for **39** (A = O). The two exceptional selenium(II) structures in this regard are **42**, with C–Se $\cdots$ O =  $144.9^\circ$ , and **44** with C–Se $\cdots$ O =  $138.9^\circ$ . These, along with **43** mentioned above, feature concatenated, strained rings which readily account for the observed deviations. For the five zero-dimensional selenium(VI) structures featuring a  $\{\cdots\text{Se}=\text{O}\}_2$  core, the Se=O $\cdots$ Se angles range from  $105.3^\circ$ , for **55**, to  $111.5^\circ$  for **53**, and the A–Se $\cdots$ O angles range from  $167.5^\circ$ , for **55** (A = O), to  $174.1^\circ$ , for **51** (A = C). The  $\{\cdots\text{Se}=\text{O}\}_2$  core also features in eight one-dimensional aggregation patterns and present narrow ranges for both Se=O $\cdots$ Se, i.e.  $94.6^\circ$  (**168**) to  $108.6^\circ$  (**165**), and A–Se $\cdots$ O angles, i.e.  $156.2^\circ$  (**165**, A = O) to  $176.8^\circ$  (**164**, A = C).

From the A–Se $\cdots$ O data included in Appendix A, it is a generalisation that the angle about the selenium atom, regardless of oxidation state, generally lies between  $140$  and  $180^\circ$ . While this observation is consistent with expectation in terms of the s-hole model to explain the nature of these interactions [45-47,251]. Taking the sub-set of 29 zero-dimensional selenium(II) examples where the selenium atom forms one Se $\cdots$ O interaction only, there are two exceptional structures where A–Se $\cdots$ O lies between  $127$  and  $128^\circ$ , i.e. **8** and **22**. Indeed, 21 examples have A–Se $\cdots$ O  $> 160^\circ$ . It might be concluded that while to a first approximation,

there is a general understanding of the mode of bonding leading to Se $\cdots$ O and related secondary bonding interactions, further investigations, such high-level crystallographic, including charge density studies and analysis [11,252,253], along with reliable computational chemistry studies [254-256] are required in order to gain a more complete picture of Se $\cdots$ O interactions. Also of interest would be the determination, experimental and theoretical, of the energies of stabilisation provided by specific Se $\cdots$ O contacts. Thus far, these are comparatively rare, e.g. 10-40 kJ/mol for molecules based on the Ebselen<sup>TM</sup> (**89** & **90**) structure [11], i.e. as noted previously [54], an energy in the range observed for conventional hydrogen bonding interactions.

Finally, while the focus of the present review has been upon the identification of intermolecular Se $\cdots$ O interactions in crystals of molecular selenium compounds, the relevance of Se $\cdots$ O secondary bonding interactions in the biological context was alluded to in the Introduction. With the present covid-19 pandemic confronting the World, it is not surprising that Ebselen<sup>TM</sup> and analogues have already been evaluated as potential inhibitors of the active site of the main protease (M<sup>Pro</sup>) of the severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) [257] in a classic case of drug repurposing [258]. On-going crystallographic, spectroscopic, e.g. <sup>77</sup>Se NMR [258], and computational studies [259,260] should also be alert for the potential influence of Se $\cdots$ O interactions in providing stability to poses adopted by selenium compounds in relevant active sites.

## 9. Conclusions

Chalcogen bonding of the type Se $\cdots$ O contribute to the stability of crystals where they can form and are shown to sustain a full range of supramolecular aggregates: any complete analysis of the molecular packing of relevant compounds should include an analysis of these and other secondary bonding interactions. In the same way, any evaluations of the biological mechanisms of action, catalytic processes, rationalisation of chemical reactivity, etc. should be

on the alert to the possible role of Se $\cdots$ O secondary bonding. Most notably by the prevalence of linear A–Se $\cdots$ O angles, for A = C, N, S and Se, the concept of the  $\sigma$ -hole provides a key impetus for the rationalisation of these interactions for selenium(II)- and selenium(IV)-containing compounds in the above contexts. However, further studies are required, both experimental and computational, for a more complete understanding of the formation of Se $\cdots$ O interactions and the energies of their association.

### **Conflict of Interest**

The author declares no conflict of interest.

### **Acknowledgements**

The author gratefully acknowledges Sunway University Sdn Bhd (Grant no. STR-RCTR-RCCM-001-2019) for support of crystallographic studies.

### **Appendix A. Supplementary data**

Supplementary data associated with this article (details of crystals featuring Se $\cdots$ O chalcogen bonding interactions: composition, diagram, distance and angle data, citation and commentary) can be found, in the online version, at doi:10.1016/j.ccr.20201.xx.xxx.

### **References**

- [1] T.C. Stadtman, Ann. Rev. Biochem. 65 (1996) 83–100; doi: [org/10.1146/annurev.bi.65.070196.000503](https://doi.org/10.1146/annurev.bi.65.070196.000503)
- [2] V.N. Gladyshev, D. L. Hatfield, J. Biomed. Sci. 6 (1999) 151–160; doi: [org/10.1159/000025383](https://doi.org/10.1159/000025383)

- [3] IUPAC-IUBMB Joint Commission on Biochemical Nomenclature (JCBN) and Nomenclature Committee of IUBMB (NC-IUBMB), *Eur. J. Biochem.* 264 (1999) 607–609.
- [4] J. Nordberg, E.S.J. Arnér, *Free Radic. Biol. Med.* 31 (2001) 1287–1312; doi: 10.1016/S0891-5849(01)00724-9
- [5] A.C. Bianco, D. Salvatore, B. Gereben, M.J. Berry, P.R. Larsen, *Endocr. Rev.* 23 (2002) 38–89; doi: 10.1210/edrv.23.1.0455
- [6] M. Allingstrup, A. Afshari, *Cochrane Database Syst. Rev.* (2015) CD003703; doi: 10.1002/14651858.CD003703.pub3
- [7] E.R.T. Tiekink, *Dalton Trans.* 41 (2012) 6390–6395; doi: 10.1039/c2dt12225a
- [8] H.-L. Seng, E.R.T. Tiekink, *Appl. Organomet. Chem.* 26 (2012) 655–662; doi: 10.1002/aoc.2928
- [9] N.V. Barbosa, C.W. Nogueira, P.A. Nogara, A.F. de Bem, M. Aschner, J.B.T. Rocha, *Metallomics* 9 (2017) 1703–1734; doi: 10.1039/c7mt00083a
- [10] Z. Chen, H. Lai, L. Hou, T. Chen, *Chem. Commun.* 56 (2020) 179–196; doi: org/10.1039/C9CC07683B
- [11] S.P. Thomas, K. Satheeshkumar, G. Mugesh, T.N. Guru Row, *Chem. Eur. J.* 21 (2015) 6793–6800; doi: org/10.1002/chem.201405998
- [12] H. Wang, J. Liu, W. Wang, *Phys. Chem. Chem. Phys.* 20 (2018) 5227–5234; doi: 10.1039/c7cp08215k
- [13] W. Wang, B. Ji, Y. Zhang, *J. Phys. Chem. A* 113 (2009) 8132–8135; doi: org/10.1021/jp904128b
- [14] C.B. Aakeröy, D.L. Bryce, G.R. Desiraju, A. Frontera, A.C. Legon, F. Nicotra, K. Rissanen, S. Scheiner, G. Terraneo, P. Metrangolo, G. Resnati, *Pure Appl. Chem.* 91 (2019) 1889–1892; doi: org/10.1515/pac-2018-0713
- [15] R.M. Minyaev, V.I. Minkin, *Can. J. Chem.* 76 (1998) 776–778; doi: 10.1139/v98-080

- [16] R.J. Fick, G.M. Kroner, B. Nepal, R. Magnani, S. Horowitz, R.L. Houtz, S. Scheiner, R.C. Trievel, *ACS Chem. Biol.* 11 (2016) 748–754; doi: [org/10.1021/acscchembio.5b00852](https://doi.org/10.1021/acscchembio.5b00852)
- [17] S. Mondal, G. Mugesh, *Chem. Eur. J.* 25 (2019) 1773–1780; doi: [org/10.1002/chem.201805112](https://doi.org/10.1002/chem.201805112)
- [18] S.P. Thomas, V. Kumar, K. Alhameedi, T.N.G. Guru Row, *Chem. Eur. J.* 25 (2019) 3591–3597; doi: [org/10.1002/chem.201805131](https://doi.org/10.1002/chem.201805131)
- [19] N. Biot, D. Bonifazi, *Coord. Chem. Rev.* 413 (2020) 213243, doi: [org/10.1016/j.ccr.2020.213243](https://doi.org/10.1016/j.ccr.2020.213243)
- [20] S. Scheiner, M. Michalczyk, W. Zierkiewicz, *Coord. Chem. Rev.* 405 (2020) 213136; doi: [org/10.1016/j.ccr.2019.213136](https://doi.org/10.1016/j.ccr.2019.213136)
- [21] M.S. Taylor, *Coord. Chem. Rev.* 413 (2020) 213270; doi: [org/10.1016/j.ccr.2020.213270](https://doi.org/10.1016/j.ccr.2020.213270)
- [22] E. Navarro-García, B. Galmés, M.D. Velasco, A. Frontera, A. Caballero, *Chem. Eur. J.* 26 (2020) 4706–4713; doi: [org/10.1002/chem.201905786](https://doi.org/10.1002/chem.201905786)
- [23] P. Wonner, T. Steinke, L. Vogel, S.M. Huber, *Chem. Eur. J.* 26 (2020) 1258–1262; doi: [org/10.1002/chem.201905057](https://doi.org/10.1002/chem.201905057)
- [24] C.M. Young, A. Elmi, D.J. Pascoe, R.K. Morris, C. McLaughlin, A.M. Woods, A.B. Frost, A. de la Houpliere, K.B. Ling, T.K. Smith, A.M.Z. Slawin, P.H. Willoughby, S.L. Cockcroft, A.D. Smith, *Angew. Chem. Int. Ed.* 59 (2020) 3705–3710; doi: [org/10.1002/anie.201914421](https://doi.org/10.1002/anie.201914421)
- [25] K.T. Mahmudov, M.N. Kopylovich, M.F.C. Guedes da Silva, A.J.L. Pombeiro, *Dalton Trans.* 46 (2017) 10121–10138; doi: [10.1039/c7dt01685a](https://doi.org/10.1039/c7dt01685a)
- [26] M. Fourmigué, A. Dhaka, *Coord. Chem. Rev.* 403 (2020) 213084; doi: [10.1016/j.ccr.2019.213084](https://doi.org/10.1016/j.ccr.2019.213084)
- [27] S. Scheiner, *Int. J. Quantum Chem.* 113 (2013) 1609–1620; doi: [10.1002/qua.24357](https://doi.org/10.1002/qua.24357)

- [28] R. Gleiter, G. Haberhauer, D.B. Werz, *Chem. Rev.* 118 (2018) 2010–2041; doi: 10.1021/acs.chemrev.7b00449
- [29] L. Vogel, P. Wonner, S.M. Huber, *Angew. Chem. Int. Ed.* 58 (2019) 1880–1891; doi: 10.1002/anie.201809432
- [30] P. Scilabra, G. Terraneo, G. Resnati, *Acc. Chem. Res.* 52 (2019) 1313–1324; doi: org/10.1021/acs.accounts.9b00037
- [31] A.C. Legon, *Phys. Chem. Chem. Phys.* 19 (2017) 14884–14896; doi: 10.1039/c7cp02518a
- [32] M. Juanes, R.T. Saragi, W. Caminati, A. Lesarri, *Chem. Eur. J.* 25 (2019) 11402–11411; doi: org/10.1002/chem.201901113
- [33] V. Kumar, Y. Xu, C. Leroy, D.L. Bryce, *Phys. Chem. Chem. Phys.* 22 (2020) 3817–3824; doi: org/10.1039/C9CP06267J
- [34] H.A. Bent, *Chem. Rev.* 68 (1968) 587–648; doi: 10.1021/cr60255a003
- [35] O. Hassel, *Science* 170 (1970) 497–502; doi: 10.1126/science.170.3957.497
- [36] N.W. Alcock, *Adv. Inorg. Chem. Radiochem.* 15 (1972) 1–58; doi: 10.1016/S0065-2792(08)60016-3
- [37] N.W. Alcock, *Bonding and Structure: Structural Principles in Inorganic and Organic Chemistry*, Ellis Horwood, New York, 1990.
- [38] P. Pyykkö, *Chem. Rev.* 97 (1997) 597–636; doi: org/10.1021/cr940396v
- [39] I. Haiduc, *Coord. Chem. Rev.* 158 (1997) 325–358; doi: org/10.1016/S0010-8545(97)90063-1
- [40] I. Haiduc, in: J.L. Attwood, J.W. Steed (Eds.), *Encyclopaedia of Supramolecular Chemistry*, vol. 2, Marcel Dekker, New York, 2004, p. 1215–1224.
- [41] N.W. Alcock, R. Countryman, *Acta Crystallogr., Section A* 13 (1975) S62.

- [42] N.W. Alcock, R.M. Countryman, *J. Chem. Soc., Dalton Trans.* (1977) 217–219; doi: [org/10.1039/DT9770000217](https://doi.org/10.1039/DT9770000217)
- [43] J. Starbuck, N.C. Norman, A.G. Orpen, *New. J. Chem.* 23 (1999) 969–972; doi: [org/10.1039/A906352H](https://doi.org/10.1039/A906352H).
- [44] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *Chem. Rev.* 116 (2016) 2478–2601; doi: [org/10.1021/acs.chemrev.5b00484](https://doi.org/10.1021/acs.chemrev.5b00484)
- [45] J.S. Murray, P. Lane, T. Clark, P. Politzer, *J. Mol. Model.* 13 (2007) 1033–1038; doi: [10.1007/s00894-007-0225-4](https://doi.org/10.1007/s00894-007-0225-4)
- [46] P. Politzer, J.S. Murray, *Crystals* 7 (2017) 212; doi: [org/10.3390/cryst7070212](https://doi.org/10.3390/cryst7070212)
- [47] M.H. Kolář, P. Hobza, *Chem. Rev.* 116 (2016) 5155–5187; doi: [10.1021/acs.chemrev.5b00560](https://doi.org/10.1021/acs.chemrev.5b00560)
- [48] D.J. Pascoe, K.B. Ling, S.L. Cockroft, *J. Am. Chem. Soc.* 139 (2017) 15160–15167; doi: [10.1021/jacs.7b08511](https://doi.org/10.1021/jacs.7b08511)
- [49] S. Scheiner, *J. Phys. Chem. A* 121 (2017) 5561–5568; doi: [10.1021/acs.jpca.7b05300](https://doi.org/10.1021/acs.jpca.7b05300)
- [50] W. Dong, Q. Li, S. Scheiner, *Molecules* 23 (2018) 1681; doi: [10.3390/molecules23071681](https://doi.org/10.3390/molecules23071681)
- [51] J.D. Velásquez, G. Mahmoudi, E. Zangrando, A.V. Gurbanov, F.I. Zubkov, Y. Zorlu, A. Masoudias, J. Echeverría, *CrystEngComm* 21 (2019) 6018–6025; doi: [org/10.1039/C9CE00959K](https://doi.org/10.1039/C9CE00959K)
- [52] J.S. Murray, P. Politzer, *Crystals* 10 (2020) 76; doi: [10.3390/cryst10020076](https://doi.org/10.3390/cryst10020076)
- [53] B. Galmés, A. Juan-Bals, A. Frontera, G. Resnati, *Chem. Eur. J.* 26 (2020) 4599–4606; doi: [org/10.1002/chem.201905498](https://doi.org/10.1002/chem.201905498)
- [54] E.R.T. Tiekink, *Coord. Chem. Rev.* 345 (2017) 219–228; doi: [org/10.1016/j.ccr.2017.01.009](https://doi.org/10.1016/j.ccr.2017.01.009)

- [55] D.P. Malenov, G.V. Janjia, V.B. Medakovic, M.B. Hall, S.D. Zarić, *Coord. Chem. Rev.* 345 (2017) 318–341; doi: [org/10.1016/j.ccr.2016.12.020](https://doi.org/10.1016/j.ccr.2016.12.020)
- [56] E.R.T. Tiekink, *CrystEngComm* 5 (2003) 101–113; doi: [org/10.1039/B301318A](https://doi.org/10.1039/B301318A)
- [57] M.A. Buntine, F.J. Kosovel, E.R.T. Tiekink, *CrystEngComm* 5 (2003) 331–336; doi: [org/10.1039/B308922C](https://doi.org/10.1039/B308922C)
- [58] Y. Liu, E.R.T. Tiekink, *CrystEngComm* 7 (2005) 20–27; doi: [org/10.1039/B416493H](https://doi.org/10.1039/B416493H)
- [59] E.R.T. Tiekink, *CrystEngComm* 8 (2006) 104–118; doi: [org/10.1039/B517339F](https://doi.org/10.1039/B517339F)
- [60] C.S. Lai, E.R.T. Tiekink, *Z. Kristallogr. Cryst. Mater.* 222 (2007) 532–538; doi: [10.1524/zkri.2007.222.10.532](https://doi.org/10.1524/zkri.2007.222.10.532)
- [61] E.R.T. Tiekink, *Appl. Organomet. Chem.* 22 (2008) 533–550; doi: [org/10.1002/aoc.1441](https://doi.org/10.1002/aoc.1441)
- [62] E.R.T. Tiekink, J. Zukerman-Schpector, *Coord. Chem. Rev.* 254 (2010) 46–76; doi: [org/10.1016/j.ccr.2009.09.007](https://doi.org/10.1016/j.ccr.2009.09.007)
- [63] E.R.T. Tiekink, *Crystals* 8 (2018) 292; doi: [org/10.3390/cryst8070292](https://doi.org/10.3390/cryst8070292)
- [64] S.M. Lee, P.J. Heard, E.R.T. Tiekink, *Coord. Chem. Rev.* 375 (2018) 410–423; doi: [org/10.1016/j.ccr.2018.03.001](https://doi.org/10.1016/j.ccr.2018.03.001)
- [65] R. Taylor, P.A. Wood, *Chem. Rev.* 119 (2019) 9427–9477; doi: [org/10.1021/acs.chemrev.9b00155](https://doi.org/10.1021/acs.chemrev.9b00155)
- [66] I.J. Bruno, J.C. Cole, P.R. Edgington, M. Kessler, C.F. Macrae, P. McCabe, J. Pearson, R. Taylor, *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.* 58 (2002) 389–397; doi: [org/10.1107/S0108768102003324](https://doi.org/10.1107/S0108768102003324)
- [67] A. Spek, *Acta Crystallogr., Sect. E: Cryst. Commun.* 76 (2020) 1–11; doi: [org/10.1107/S2056989019016244](https://doi.org/10.1107/S2056989019016244)



- [68] C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. I. Platings, G. P. Shields, J. S. Stevens, M. Towler and P. A. Wood, *J. Appl. Crystallogr.* 2020, **53**, 226–235; doi: 10.1107/S1600576719014092
- [69] K. Brandenburg, DIAMOND. Visual Crystal Structure Information System, version 3.1, Crystal Impact, Bonn, Germany, 2006.
- [70] F. Wang, P.L. Polavarapu, J. Drabowicz, P. Kielbasinski, M.J. Potrzebowski, M. Mikołajczyk, M.W. Wieczorek, W.W. Majzner, I. Łażewska, *J. Phys. Chem. A* 108 (2004) 2072–2079; doi: 10.1021/jp031270h
- [71] P.P. Phadnis, A. Kunwar, M. Kumar, R. Mishra, A. Wadawale, K.I. Priyadarsini, V.K. Jain, *J. Organomet. Chem.* 852 (2017) 1–7; doi: 10.1016/j.jorganchem.2017.09.029
- [72] S. Goswami, A. Hazra, R. Chakrabarty, H.-K. Fun, *Org. Lett.* 11 (2009) 4350–4353; doi: 10.1021/ol901737s
- [73] M. Ruamps, N. Lugan, V. Cesar, *Eur. J. Inorg. Chem.* (2017) 4167–4173; doi: 10.1002/ejic.201700883
- [74] E. Block, E.V. Dikarev, R.S. Glass, J. Jin, B. Li, X. Li, S.-Z. Zhang, *J. Am. Chem. Soc.* 128 (2006) 14949–14961; doi: 10.1021/ja065037j
- [75] J.Y. See, H. Yang, Y. Zhao, M.W. Wong, Z. Ke, Y.-Y. Yeung, *ACS Catalysis* 8 (2018) 850–858; doi: 10.1021/acscatal.7b03510
- [76] G. Hua, J. Du, A.M.Z. Slawin, J.D. Woollins, *J. Org. Chem.* 79 (2014) 3876–3886; doi: 10.1021/jo500316v
- [77] A.M. Toma, A. Nicoară, A. Silvestru, T. Rüffer, H. Lang, M. Mehring, *J. Organomet. Chem.* 810 (2016) 33–39; doi: 10.1016/j.jorganchem.2016.03.002
- [78] C. Allen, J.C.A. Boeyens, A.G. Briggs, L. Denner, A.J. Markwell, D.H. Reid, B.G. Rose, *J. Chem. Soc. Chem. Comm.* (1987) 967–968; doi: 10.1039/C39870000967

- [79] M. Iyoda, R. Watanabe, Y. Miyake, *Chem. Lett.* 33 (2004) 570–571; doi: 10.1246/cl.2004.570
- [80] P. Bhattacharyya, A.M.Z. Slawin, J.D. Woollins, *Chem. Eur. J.* 8 (2002) 2705–2711; doi: 10.1002/1521-3765(20020617)8:12<2705::AID-CHEM2705>3.0.CO;2-2
- [81] G. Karabanovich, J. Roh, . Padělková, Z. Novák, K. Vávrová, Z.A. Hrabálek, *Tetrahedron* 69 (2013) 8798–8808; doi: 10.1016/j.tet.2013.07.103
- [82] B. M. Laloo, H. Mecadon, Md. R. Rohman, I. Kharbangar, I. Kharkongor, M. Rajbangshi, R. Nongkhlaw, B. Myrboh, *J. Org. Chem.* 77 (2012) 707–712; doi: 10.1021/jo201985n
- [83] C. Gicquel-Mayer, G. Perez, P. Lerouge, C. Paulmier, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 43 (1987) 284–287; doi: 10.1107/S0108270187096112
- [84] V. Kubát, M. Babiak, Z. Trávníček, J. Novosad, *Polyhedron* 124 (2017) 62–67; doi: 10.1016/j.poly.2016.12.034
- [85] P. Arsenyan, E. Paegle, S. Belyakov, *Chem. Heterocycl. Compd.* 49 (2013) 791–796; doi: 10.1007/s10593-013-1310-5
- [86] P. Arsenyan, E. Vasiljeva, S. Belyakov, *Chem. Heterocycl. Compd.* 47 (2011) 237–241; doi: 10.1007/s10593-011-0746-8
- [87] K.M. Aumann, P.J. Scammells, J.M. White, C.H. Schiesser, *Org. Biomol. Chem.* 5 (2007) 1276–1281; doi: 10.1039/b700812k
- [88] X. Chen, K.-H. Baek, Y. Kim, S.-J. Kim, I. Shin, J. Yoon, *Tetrahedron* 66 (2010) 4016–4021; doi: 10.1016/j.tet.2010.04.042
- [89] K. Matoba, T. Yamazaki, *Chem. Pharm. Bull.* 35 (1987) 4967–4971; doi: 10.1248/cpb.35.4967
- [90] J. Zhou, J.-M. Huang, Y. Tang and R.-Y. Chen, *Chin. J. Struct. Chem.* 18 (1999) 103–106.

- [91] K. Satheeshkumar, G. Mugesh, *Chem. Eur. J.* 17 (2011) 4849–4857; doi: 10.1002/chem.201003417
- [92] K. Shimada, A. Moro-oka, A. Maruyama, H. Fujisawa, T. Saito, R. Kawamura, H. Kogawa, M. Sakuraba, Y. Takata, S. Aoyagi, Y. Takikawa, C. Kabuto, *Bull. Chem. Soc. Jpn.* 80 (2007) 567–577; doi: org/10.1246/bcsj.80.567
- [93] V.P. Singh, H.B. Singh, R.J. Butcher, *Chem. Commun.* 47 (2011) 7221–7223; doi: 10.1039/c1cc12152a
- [94] L. Dupont, M. Messali, L. Christiaens, *Acta Crystallogr., Sect. E: Struct. Rep. Online* 59 (2003) o547–o549; doi: 10.1107/S1600536803006433
- [95] V.P. Singh, H.B. Singh, R.J. Butcher, *Chem. Asian J.* 6 (2011) 1431–1442; doi: 10.1002/asia.201000858
- [96] F.-Y. Meng, Y.-A. Chen, C.-L. Chen, P.-T. Chou, *ChemPhotoChem* 2 (2018) 475–480; doi: 10.1002/cptc.201800066
- [97] V. Kumar, Y. Xu, D.L. Bryce, *Chem. Eur. J.* 2020, 26, 3275–3286; doi: org/10.1002/chem.201904795
- [98] G.M. Arvanitis, M.E. Berardini, D. Allardice, P.E. Dumas, *J. Chem. Cryst.* 24 (1994) 421–423; doi: 10.1007/BF01666088
- [99] A.S. Hodage, P.P. Phadnis, A. Wadawale, K.I. Priyadarsini, V.K. Jain, *Phosphorus, Sulfur, Silicon, Relat. Elem.* 189 (2014) 700–710; doi: 10.1080/10426507.2013.844144
- [100] K.P. Bhabak, G. Mugesh, *Chem. Asian J.* 4 (2009) 974–983; doi: 10.1002/asia.200800483
- [101] P. Arsenyan, E. Paegle, S. Belyakov, I. Shestakova, E. Jaschenko, I. Domracheva, J. Popelis, *Eur. J. Med. Chem.* 46 (2011) 3434–3443; doi: 10.1016/j.ejmech.2011.05.008
- [102] S. Braverman, M. Cherkinsky, Y. Kalendar, R. Jana, M. Sprecher, I. Goldberg, *Synthesis* 46 (2014) 119–125; doi: 10.1055/s-0033-1338555

- [103] Y. Kim, T. Jun, S.V. Mulay, S.T. Manjare, J. Kwak, Y. Lee, D.G. Churchill, Dalton Trans. 46 (2017) 4111–4117; doi: 10.1039/C7DT00555E
- [104] S. Hayashi, H. Wada, T. Ueno, W. Nakanishi, J. Org. Chem. 71 (2006) 5574–5585; doi: 10.1021/jo060527f
- [105] S.-C. Yu, H. Kuhn, C.-G. Daniliuc, I. Ivanov, P.G. Jones, W.-W. du Mont, Org. Biomol. Chem. 8 (2010) 828–834; doi: 10.1039/b918778b
- [106] T.M. Klapötke, B. Krumm, M. Scherr, Z. Anorg. Allg. Chem. 636 (2010) 1955–1961
- [107] T. Annaka, N. Nakata, A. Ishii, New J. Chem. 43 (2019) 11643–11652; doi: 10.1039/C9NJ02813G
- [108] T. Kawashima, F. Ohno, R. Okazaki, J. Am. Chem. Soc. 115 (1993) 10434–10435
- [109] T. Kataoka, S. Watanabe, K. Yamamoto, M. Yoshimatsu, G. Tanabe, O. Muraoka, J. Org. Chem. 63 (1998) 6382–6386; doi: 10.1021/jo980999x
- [110] E.C. Llaguno, I.C. Paul, J. Chem. Soc., Perkin Trans. 2 (1972) 2001–2006; doi: 10.1039/p29720002001
- [111] R. Betz, M. Pfister, M.M. Reichvilser, P. Klüfers, Z. Anorg. Allg. Chem. 634 (2008) 1393–1396; doi: 10.1002/zaac.200800097
- [112] T. Maaninen, T. Chivers, R. Laitinen, G. Schatte, M. Nissinen, Inorg. Chem. 39 (2000) 5341–5347; doi: 10.1021/ic000598b
- [113] P. Klüfers, M.M. Reichvilser, Eur. J. Inorg. Chem. (2008) 384–396; doi: 10.1002/ejic.200700837
- [114] T.M. Klapötke, B. Krumm, P. Mayer, H. Piotrowski, O.P. Ruscitti, Z. Naturforsch., B: Chem. Sci. 57 (2002) 145–150.
- [115] A.G. Makarov, A.Yu. Makarov, I.Yu. Bagryanskaya, M.M. Shakirov, A.V. Zibarev, J. Fluorine Chem. 144 (2012) 118–123; doi: 10.1016/j.jfluchem.2012.08.002

- [116] M. Budesinsky, V. Vanek, M. Dracinsky, R. Pohl, L. Postova-Slavetinska, V. Sychrovsky, . Picha, I. Cisarova, *Tetrahedron* 70 (2014) 3871–3886; doi: 10.1016/j.tet.2014.04.047
- [117] Z. Žák, J. Marek, L. Kezníkl, *Z. Anorg. Allg. Chem.* 622 (1996) 1101–1105; doi: 10.1002/zaac.19966220628
- [118] L. Richtera, V. Jancik, D. Martínez-Otero, A. Pokluda, Z. Zak, J. Taraba, J. Touzin, *Inorg. Chem.* 53 (2014) 6569–6577; doi: 10.1021/ic500137z
- [119] L. Richtera, J. Taraba, J. Toužín, *Z. Anorg. Allg. Chem.* 629 (2003) 716–721; doi: 10.1002/zaac.200390121
- [120] C. Ghiazza, L. Khrouz, C. Monnereau, T. Billard, A. Tlili, *Chem. Commun.* 54 (2018) 9909–9912; doi: 10.1039/C8CC05256E
- [121] P.G. Jones, A. Chrapkowski, Private Communication to the Cambridge Structural Database (2004) Refcode YADVOP
- [122] H.-Q. Wu, S.-H. Luo, L. Cao, H.-N. Shi, B.-W. Wang, Z. Wang, Private Communication to the Cambridge Structural Database (2019) Refcode VIWNAT
- [123] H.J. Traesel, P.R. Olivato, J. Valenca, D.N.S. Rodrigues, J. Zukerman-Schpector, M.D. Colle, *J. Mol. Struct.* 1157 (2018) 29–39; doi: 10.1016/j.molstruc.2017.12.040
- [124] S. Kumar, N. Sharma, I.K. Maurya, A. Verma, S. Kumar, K.K. Bhasin, R.K. Sharma, *New J. Chem.* 41 (2017) 2919–2926; doi: 10.1039/C7NJ00338B
- [125] P.S. Engl, R. Senn, E. Otth, A. Togni, *Organometallics* 34 (2015) 1384–1395; doi: 10.1021/acs.organomet.5b00137
- [126] D. Das, G. Roy, G. Muges, *J. Med. Chem.* 58 (2008) 7313–7317; doi: 10.1021/jm800894m
- [127] W.-J. Chang and C.-M. Sun, Private Communication to the Cambridge Structural Database (2012) Refcode GOHPEA

- [128] M.S. Afzal, J.-P. Pitteloud, D. Buccella, *Chem. Commun.* 50 (2014) 11358–11361; doi: 10.1039/C4CC04460F
- [129] G.A. Brown, K.M. Anderson, M. Murray, T. Gallagher, N.J. Hales, *Tetrahedron* 56 (2000) 5579–5586; doi: 10.1016/S0040-4020(00)00408-7
- [130] G. Hua, J. Du, A.M.Z. Slawin, J.D. Woollins, *Synlett* 25 (2014) 2189–2195; doi: 10.1055/s-0034-1378525
- [131] T. Laitalainen, T. Simonen, R. Kivekas, M. Klinga, *J. Chem. Soc., Perkin Trans. 1* (1983) 333–340; doi: 10.1039/p19830000333
- [132] K. Okuma, Y. Mori, T. Shigetomi, M. Tabuchi, K. Shioji, Y. Yokomori, *Tetrahedron Lett.* 48 (2007) 8311–8313; doi: 10.1016/j.tetlet.2007.09.120
- [133] S.J. Balkrishna, A.S. Hodage, S. Kumar, P. Panini, S. Kumar, *RSC Adv.* 4 (2015) 11535–11538; doi: 10.1039/C4RA00381K
- [134] M. Iwasaki, N. Miki, Y. Tsuchiya, K. Nakajima, Y. Nishihara, *Org. Lett.* 19 (2017) 1092–1095; doi: 10.1021/acs.orglett.7b00116
- [135] Y. S. Peng, H. S. Xu, P. Naumov, S.S.S. Raj, H.-K. Fun, I.A. Razak, S.W. Ng, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 56 (2000) 1386–1388; doi: 10.1107/S0108270100011276
- [136] S. Sankari, P. Sugumar, P. Manisankar, S. Muthusubramanian, M.N. Ponnuswamy, *Acta Crystallogr., Sect. E: Struct. Rep. Online* 68 (2012) o871; doi: 10.1107/S1600536812007027
- [137] K. Doudin, K.W. Tornrös, *J. Mol. Struct.* 1134 (2017) 611–616; doi: 10.1016/j.molstruc.2016.12.067
- [138] C.J. Narangoda, T.R. Lex, M.A. Moore, C.D. McMillen, A. Kitaygorodskiy, J.E. Jackson, D.C. Whitehead, *Org. Lett.* 20 (2018) 8009–8013; doi: 10.1021/acs.orglett.8b03590

- [139] S.S. Zade, S. Panda, H.B. Singh, R.B. Sunoj, R.J. Butcher, *J. Org. Chem.* 70 (2005) 3693–3704; doi: 10.1021/jo0478656
- [140] U. Flörke; Private Communication to the Cambridge Structural Database (2019)  
Refcode KIXTUI
- [141] A. Blaschette, M. Naveke, P.G. Jones, *Chem. Zeit.* 114 (1990) 384–386.
- [142] Q. Glenadel, C. Ghiazza, A. Tlili, T. Billard, *Adv. Synth. Catal.* 359 (2017) 3414–3420; doi: 10.1002/adsc.201700904
- [143] G.M. Li, R.A. Zingaro, M. Segi, J.H. Reibenspies, T. Nakajima, *Organometallics* 16 (1997) 756–762; doi: 10.1021/om960883w
- [144] M. Yamamura, T. Nabeshima, *Bull. Chem. Soc. Jpn.* 89 (2016) 42–49; doi: 10.1246/bcsj.20150288
- [145] G. Hua, J. Du, A.M.Z. Slawin, J.D. Woollins, *Chem. Sel.* 1 (2016) 6810–6817; doi: 10.1002/slct.201601577
- [146] G. Hua, J. Du, A.M.Z. Slawin, J.D. Woollins, *Molecules* 22 (2017) 46; doi: 10.3390/molecules22010046
- [147] J.-B. Shen, X. Lv, J.-F. Chen, Y.-F. Zhou, G.-L. Zhao, *Acta Crystallogr., Sect. E: Struct. Rep. Online* 67 (2011) o803; doi: 10.1107/S1600536811007185
- [148] G.L. Sommen, A. Linden, H. Heimgartner, *Tetrahedron* 62 (2006) 3344–3354; doi: 10.1016/j.tet.2006.01.077
- [149] T. Fellowes and J. M. White, *CrystEngComm* 21 (2019) 1539–1542; doi: 10.1039/C8CE01853G
- [150] L. Dupont, O. Dideberg, P. Jacquemin, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 46 (1990) 484–486; doi: 10.1107/S0108270189007894
- [151] S.-X. Feng, C.-M. Yang, J.-L. Wang, J.-Y. Ma, *Chem. Res. Appln.* 30 (2018) 840–845; doi: 10.3969/j.issn.1004-1656.2018.05.030

- [152] K. P. Bhabak, G. Mugesh, *Chem. Eur. J.* 13 (2007) 4594–4601; doi: 10.1002/chem.200601584
- [153] M. Piatek, B. Oleksyn, J. Sliwinski, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 51 (1995) 298–301; doi: 10.1107/S0108270193012983
- [154] R. Shukla, N. Claiser, M. Souhassou, C. Lecomte, S.J. Balkrishna, S. Kumar, D. Chopra, *IUCrJ* 5 (2018) 647–653; doi: 10.1107/S2052252518011041
- [155] L. Wang, Y. Xu, Z. Guo, X. Wei, *IUCrData* 2 (2017) x170532; doi: 10.1107/S2414314617005326
- [156] X. Zhu, Y. Xu, H. Han, Z. Guo, X. Wei, *Acta Crystallogr., Sect. E: Struct. Rep. Online* 69 (2013) o1538; doi: 10.1107/S1600536813024744
- [157] H. Ungati, V. Govindaraj, M. Narayanan, G. Mugesh, *Angew. Chem., Int. Ed.* 58 (2019) 8156–8160; doi: 10.1002/anie.201903958
- [158] S.J. Balkrishna, B.S. Bhakuni, D. Chopra, S. Kumar, *Org. Lett.* 12 (2010) 5394–5397; doi: 10.1021/ol102027j
- [159] M.J. Laws, C.H. Schiesser, J.M. White, S.-L. Zheng, *Aust. J. Chem.* 53 (2000) 277–283; doi: 10.1071/CH99127
- [160] S.J. Balkrishna, B.S. Bhakuni, S. Kumar, *Tetrahedron* 67 (2011) 9565–9575; doi: 10.1016/j.tet.2011.09.141
- [161] L. Dupont, P. Jacquemin, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 50 (1994) 1801–1802; doi: 10.1107/S0108270194001691
- [162] V.A. Potapov, E.O. Kurkutov, M.V. Musalov, S.V. Amosova, *Tetrahedron Lett.* 51 (2010) 5258–5261; doi: 10.1016/j.tetlet.2010.07.133
- [163] R.A. Bragg, J. Clayden, M. Bladon, O. Ichihara, *Tetrahedron Lett.* 42 (2001) 3411–3414; doi: 10.1016/S0040-4039(01)00502-0



- [164] S.E. Brantley, B. Gerlach, M.M. Olmstead, K.M. Smith, *Tetrahedron Lett.* 38 (1997) 937–940; doi: 10.1016/S0040-4039(97)00002-6
- [165] I.V. Svistunova, G.O. Tretyakova, K.A. Gayvoronskaya, *Phosphorus, Sulfur, Silicon, Relat. Elem.* 192 (2017) 1177–1187; doi: 10.1080/10426507.2017.1354210
- [166] M.B. Hursthouse, D.S. Hughes, A.L. Redfern, D.W. Knight, Private Communication to the Cambridge Structural Database (2013) Refcode TELLIH
- [167] G. Roy, P.N. Jayaram, G. Muges, *Chem. Asian J.* 8 (2013) 1910–1921; doi: 10.1002/asia.201300274
- [168] O.R. Shangpliang, B. Kshiar, K. Wanniang, I.D. Marpna, T.M. Lipon, B.M. Laloo, B. Myrboh, *J. Org. Chem.* 83 (2018) 5829–5835; doi: 10.1021/acs.joc.8b00558
- [169] J. Yu, J.-H. Kim, H.W. Lee, V. Alexander, H.-C. Ahn, W.J. Choi, J. Choi, L.S. Jeong, *Chem. Eur. J.* 19 (2013) 5528–5532; doi: 10.1002/chem.201300741
- [170] G. Adiwidjaja, O. Schulze, J. Voss, J. Wirsching, *Carbohydr. Res.* 325 (2000) 107–119; doi: 10.1016/S0008-6215(99)00321-3
- [171] Z. Majeed, W.R. McWhinnie, K. Paxton, T.A. Hamor, *J. Organomet. Chem.* 577 (1999) 15–18; doi: 10.1016/S0022-328X(98)01019-5
- [172] Y.A. Getmanenko, T.G. Allen, H. Kim, J.M. Hales, B. Sandhu, M.S. Fonari, K. Yu. Suponitsky, Y. Zhang, V.N. Khrustalev, J.D. Matichaz, T.V. Timofeeva, S. Barlow, S.-H. Chi, J.W. Perry, S.R. Marder, *Adv. Funct. Mater.* 28 (2018) 1804073; doi: 10.1002/adfm.201804073
- [173] P.C. Ho, J. Rafique, J. Lee, L.M. Lee, H.A. Jenkins, J.F. Britten, A.L. Braga, I. Vargas-Baca, *Dalton Trans.* 46 (2017) 6570–6579; doi: 10.1039/C7DT00612H
- [174] Y.-X. Xiao, X.-F. Liu, H.-S. Xu, J. Zhu Jun, Y.-Q. Huang, S.-Z. Hu, *Chin. J. Struct. Chem.* 16 (1997) 42–47.

- [175] S.J. Balkrishna, S. Kumar, G.K. Azad, B.S. Bhakuni, P. Panini, N. Ahalawat, R.S. Tomar, M.R. Detty, S. Kumar, *Org. Biomol. Chem.* 12 (2014) 1215–1219; doi: 10.1039/C4OB00027G
- [176] A. Gieren, V. Lamm, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 38 (1982) 2605–2611; doi: 10.1107/S0567740882009443
- [177] M. Sbit, L. Dupont, O. Dideberg, C. Lambert, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 44 (1988) 340–342; doi: 10.1107/S0108270187010837
- [178] S.J. Balkrishna, Ch.D. Prasad, P. Panini, M.R. Detty, D. Chopra, S. Kumar, *J. Org. Chem.* 77 (2012) 9541–9552; doi: 10.1021/jo301486c
- [179] Z.-L. Zuo, *Acta Crystallogr., Sect. E: Struct. Rep. Online* 69 (2013) o636; doi: 10.1107/S1600536813007526
- [180] I. Trentin, C. Schindler, C. Schulzke, *Acta Crystallogr., Sect. E: Cryst. Commun.* 74 (2018) 840–845; doi: 10.1107/S2056989018007454
- [181] K. Sivapriya, P. Suguna, S. Shubashree, P.R. Sridhar, S. Chandrasekaran, *Carbohydr. Res.* 342 (2007) 1151–1158; doi: 10.1016/j.carres.2007.02.035
- [182] D. Sureshkumar, S. Koutha, S. Chandrasekaran, *Eur. J. Org. Chem.* (2007) 4543–4551; doi: 10.1002/ejoc.200700357
- [183] P. Kuronen, T. Laitalainen, O. Orama, *J. Heterocycl. Chem.* 30 (1993) 961–965; doi: 10.1002/jhet.5570300420
- [184] J.T. Lowe, A. Chandrasekaran, R.O. Day, W. Rosen, *Chem. Commun.* (2001) 1390–1391; doi: 10.1039/b103499p
- [185] R.J. Adrien, R.W. Gable, B.F. Hoskins, D. Dakternieks, *J. Organomet. Chem.* 359 (1989) 33–39; doi: 10.1016/0022-328X(89)85248-9
- [186] O. Foss, F. Kvammen, K. Marøy, *J. Chem. Soc., Dalton Trans.* (1985) 231–237; doi: 10.1039/dt9850000231

- [187] E.A. Meyers, R.A. Zingaro, N.L.M. Dereu, Z. Kristallogr. Cryst. Mater. 210 (1995) 305; doi: 10.1524/zkri.1995.210.4.305
- [188] S. Kumar, S. Panda, H.B. Singh, G. Wolmershäuser, R.J. Butcher, Struct. Chem. 18 (2007) 127–132; doi: 10.1007/s11224-006-9082-5
- [189] A.S. Hodage, P.P. Phadnis, A. Wadawale, K.I. Priyadarsini, V.K. Jain, Anal. Sci.: X-Ray Struct. Anal. Online 25 (2009) 101–102; doi: 10.2116/xraystruct.25.101
- [190] D. Sureshkumar, V. Ganesh, S. Chandrasekaran, J. Org. Chem. 72 (2007) 5313–5319; doi: 10.1021/jo070705k
- [191] D.R. Garud, M. Koketsu, M. Ebihara, H. Ishihara, Acta Crystallogr., Sect. E: Struct. Rep. Online 62 (2006) o2133–o2134; doi: 10.1107/S1600536806015212
- [192] A. Chesney, M.R. Bryce, M.A. Chalton, A.S. Batsanov, J.A.K. Howard, J.-M. Fabre, L. Binet, S. Chakroune, J. Org. Chem. 61 (1996) 2877–2881; doi: 10.1021/jo951979n
- [193] D.M. Freudendahl, M. Iwaoka, T. Wirth, Eur. J. Org. Chem. (2010) 3934–3944; doi: 10.1002/ejoc.201000514
- [194] M.J. Potrzebowski, M. Michalska, J. Blaszczyk, M.W. Wieczorek, W. Ciesielski, S. Kazmierski, J. Pluskowski, J. Org. Chem. 60 (1995) 3139–3148; doi: 10.1021/jo00115a033
- [195] J. Hildebrandt, T. Niksch, R. Trautwein, N. Häfner, H. Görls, M.-C. Barth, M. Dürst, I.B. Runnebaum, W. Weigand, Phosphorus, Sulfur, Silicon, Relat. Elem. 192 (2017) 182–186; doi: 10.1080/10426507.2016.1250760
- [196] A. Linden, Y. Zhou, H. Heimgartner, Acta Crystallogr., Sect. C: Cryst. Struct. Chem. 70 (2014) 482–487; doi: 10.1107/S2053229614008237
- [197] M.W. Carland, C.H. Schiesser, J.M. White, Aust. J. Chem. 57 (2004) 97–100; doi: 10.1071/CH03210
- [198] C.P. Prabhu, P.P. Phadnis, A.P. Wadawale, K.I. Priyadarsini, V.K. Jain, J. Organomet. Chem. 713 (2012) 42–50; doi: 10.1016/j.jorganchem.2012.04.014

- [199] G.D. Morris, F.W.B. Einstein, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 42 (1986) 1433–1435; doi: 10.1107/S0108270186092004
- [200] P. Maity, D. Kundu, R. Roy, B.C. Ranu, *Org. Lett.* 16 (2014) 4122–4125; doi: 10.1021/ol501820e
- [201] G. Cooke, M.R. Bryce, M.C. Petty, D.J. Ando, M.B. Hursthouse, *Synthesis* (1993) 465–467; doi: 10.1055/s-1993-25881
- [202] P. Kumar, V.S. Kashid, J.T. Mague, M.S. Balakrishna, *Tetrahedron Lett.* 55 (2014) 5232–5235; doi: 10.1016/j.tetlet.2014.08.005
- [203] T. Shirahata, M. Kibune, H. Yoshino, T. Imakubo, *Chem. Eur. J.* 13 (2007) 7619–7630; doi: 10.1002/chem.200700314
- [204] T. Imakubo, T. Shirahata, M. Kibune, *Chem. Commun.* (2004) 1590–1591; doi: 10.1039/b403559c
- [205] K. Sivapriya, P. Suguna, S. Chandrasekaran, *Tetrahedron Lett.* 48 (2007) 2091–2095; doi: 10.1016/j.tetlet.2007.01.128
- [206] J. Beckmann, A. Duthie, *Z. Anorg. Allg. Chem.* 631 (2005) 1849–1855; doi: 10.1002/zaac.200500167
- [207] A.S. Filatov, E. Block, M.A. Petrukhina, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 61 (2005) o596–o598; doi: 10.1107/S0108270105027587
- [208] V.P. Singh, J.-F. Poon, R.J. Butcher, L. Engman, *Chem. Eur. J.* 20 (2014) 12563–12571; doi: 10.1002/chem.201403229
- [209] H. Ge, Q. Shen, *Org. Chem. Front.* 6 (2019) 2205–2209; doi: 10.1039/C8QO01249K
- [210] D. Dakternieks, R.W. Gable, B.F. Hoskins, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 45 (1989) 206–208; doi: 10.1107/S0108270188011126
- [211] J. Toužín, K. Nepelchová, Z. Žák, M. Černík, *Collect. Czech. Chem. Commun.* 67 (2002) 577–586; doi: 10.1135/cccc20020577

- [212] B. Dahlén, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 30 (1974) 647–651; doi: 10.1107/S0567740874003463
- [213] P.R. Prasad, H.B. Singh, R.J. Butcher, *Molecules* 20 (2015) 12670–12685; doi: 10.3390/molecules200712670
- [214] N. Kamigata, Y. Nakamura, K. Kikuchi, I. Ikemoto, T. Shimizu, H. Matsuyama, J. Chem. Soc., *Perkin Trans. 1* (1992) 1721–1728; doi: 10.1039/p19920001721
- [215] T. Takahashi, N. Nakao, T. Koizumi, *Tetrahedron: Asymm.* 8 (1997) 3293–3308; doi: 10.1016/S0957-4166(97)00423-0
- [216] Y. Nakahima, T. Shimizu, K. Hirabayashi, N. Kamigata, M. Yasui, M. Nakazato, F. Iwasaki, *Tetrahedron Lett.* 45 (2004) 2301–2303; doi: 10.1016/j.tetlet.2004.01.107
- [217] D.S. Lamani, D. Bhowmick, G. Mugesh, *Org. Biomol. Chem.* 10 (2012) 7933–7943; doi: 10.1039/c2ob26156a
- [218] K. Maartmann-Moe, K.A. Sanderud, J. Songstad, *Acta Chem. Scand.* 38 (1984) 187–200; doi: 10.3891/acta.chem.scand.38a-0187
- [219] M.R. Detty, H.R. Luss, *Organometallics* 11 (1992) 2157–2162; doi: 10.1021/om00042a032
- [220] T.G. Back, B.P. Dyck, S. Nan, M. Parvez, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 54 (1998) 425–427; doi: 10.1107/S0108270197015916
- [221] X. Yan, R. Long, F. Luo, L. Yang, X. Zhou, *Tetrahedron Lett.* 58 (2017) 54–58; doi: 10.1016/j.tetlet.2016.11.098
- [222] D.B. Werz, R. Gleiter, F. Rominger, *Eur. J. Org. Chem.* (2003) 151–154; doi: [https://doi.org/10.1002/1099-0690\(200301\)2003:1<151::AID-EJOC151>3.0.CO;2-7](https://doi.org/10.1002/1099-0690(200301)2003:1<151::AID-EJOC151>3.0.CO;2-7)
- [223] R. Kivekas, T. Laitalainen, T. Simonen, *Acta Chem. Scand.* 40 (1986) 98–100; doi: 10.3891/acta.chem.scand.40b-0098

- [224] L. Boudiba, L. Ouahab, A. Gouasmia, *Tetrahedron Lett.* 47 (2006) 3123–3125; doi: 10.1016/j.tetlet.2006.02.145
- [225] C. Schindler, C. Schulzke, *Inorg. Chem. Commun.* 77 (2017) 80–82; doi: 10.1016/j.inoche.2017.02.005
- [226] G. Hua, A.L. Fuller, A.M.Z. Slawin, J.D. Woollins, *Eur. J. Org. Chem.* (2010) 2607–2615; doi: 10.1002/ejoc.201000075
- [227] R. Kapoor, P. Wadhawan, P. Kapoor, J.F. Sawyer, *Can. J. Chem.* 66 (1988) 2367–2374; doi: 10.1139/v88-374
- [228] S.K. Tripathi, U. Patel, D. Roy, R.B. Sunoj, H.B. Singh, G. Wolmershäuser, R.J. Butcher, *J. Org. Chem.* 70 (2005) 9237–9247; doi: 10.1021/jo051309+
- [229] S. Claeson, V. Langer, S. Allenmark, *Chirality* 12 (2000) 71–75; doi: 10.1002/(SICI)1520-636X(2000)12:2<71::AID-CHIR3>3.0.CO;2-S
- [230] B. Dahlen, B. Lindgren, *Acta Chem. Scand.* 33 (1979) 403–405; doi: 10.3891/acta.chem.scand.33a-0403
- [231] T. Maaninen, R. Laitinen, T. Chivers, *Chem. Commun.* (2002) 1812–1813; doi: 10.1039/b205011k
- [232] J. Beck, P. Krieger-Beck, K. Kelm, *Z. Naturforsch., B: Chem. Sci.* 61 (2006) 123–132.
- [233] H.-Y. Li, H.-F. Han, W.-J. Li, X.-H. Wei, *Chin. J. Struct. Chem.* 31 (2012) 910–914.
- [234] G. L. Sommen, A. Linden, H. Heimgartner, *Helv. Chim. Acta* 90 (2007) 641–651; doi: 10.1002/hlca.200790067
- [235] O. Jeannin, H.-T. Huynh, A.M.S. Riel, M. Fourmigué, *New J. Chem.* 42 (2018) 10502–10509; doi: 10.1039/C8NJ00554K
- [236] S. Aboulkacem, D. Naumann, W. Tyrre, I. Pantenburg, *Organometallics* 31 (2012) 1559–1565; doi: 10.1021/om201195j

- [237] P. Arsenyan, J. Vasiljeva, S. Belyakov, E. Liepinsh, M. Petrova, *Eur. J. Org. Chem.* (2015) 5842–5855; doi: 10.1002/ejoc.201500582
- [238] T.M. Klapötke, B. Krumm, K. Polborn, *Eur. J. Inorg. Chem.* (1999) 1359–1366; doi: 10.1002/(SICI)1099-0682(199908)1999:8<1359::AID-EJIC1359>3.3.CO;2-3
- [239] N. W. Alcock, J. F. Sawyer, *Dalton Trans.* (1980) 115–120; doi: 10.1039/dt9800000115
- [240] S. Fritz, C. Ehm, D. Lentz, *Inorg. Chem.* 54 (2015) 5220–5231; doi: 10.1021/acs.inorgchem.5b00107
- [241] K. Eichstaedt, A. Wasilewska, B. Wicher, M. Gdaniec, T. Polonski, *Cryst. Growth Des.* 16 (2016) 1282–1293; doi: 10.1021/acs.cgd.5b01356
- [242] K. Legin, A.A. Leitch, A. Assoud, W. Yong, J. Desmarais, J.S. Tse, S. Desgreniers, R.A. Secco, R.T. Oakley, *Inorg. Chem.* 57 (2018) 4757–4770; doi: 10.1021/acs.inorgchem.8b00485
- [243] M.A. Nascimento, E. Heyer, J.J. Clarke, H.J. Cowley, A. Alberola, N. Stephaniuk, J.M. Rawson, *Angew. Chem., Int. Ed.* 58 (2018) 1371–1375; doi: 10.1002/anie.201812132
- [244] A.M.S. Riel, O. Jeannin, O.B. Berryman, M. Fourmigué, *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mat.* 75 (2019) 34–38; doi: 10.1107/S2052520618017778
- [245] J.D. Dunitz, R. Taylor, *Chem. Eur. J.* 3 (1997) 89–98; doi: org/10.1002/chem.19970030115
- [246] E.R.T. Tiekink, J. Zukerman-Schpector, *CrystEngComm* 11(2009) 2701–2711; doi: org/10.1039/B910209D
- [247] I. Caracelli, I. Haiduc, J. Zukerman-Schpector, E.R.T. Tiekink, *Coord. Chem. Rev.* 257 (2013) 2863–2879; doi: org/10.1016/j.ccr.2013.05.022
- [248] I. Caracelli, J. Zukerman-Schpector, E.R.T. Tiekink, *Coord. Chem. Rev.* 256 (2012) 412–438; doi: 10.1016/j.ccr.2011.10.021

- [249] I.S. Đorđević, M. Popadić, M. Sarvan, M. Petković-Benazzouz, G.V. Janjić, *Acta Crystallogr., Sect. B, Struct. Sci., Cryst. Eng. Mater.* 76 (2020) 122–136; doi: 10.1107/S2052520619016287
- [250] E.R.T. Tiekink, *Crystals* 10 (2020) article no. 503; doi: <https://doi.org/10.3390/cryst10060503>
- [251] T. Clark, M. Hennemann, J.S. Murray, P. Politzer, *P. J. Mol. Model.* 13 (2007) 291–296; doi: [org/10.1007/s00894-006-0130-2](https://doi.org/10.1007/s00894-006-0130-2)
- [252] M.E. Brezgunova, J. Lieffrig, E. Aubert, S. Dahaoui, P. Fertey, S. Lebègue, J.G. Ángyán, M. Fourmigué, E. Espinosa, *Cryst. Growth Des.* 13 (2013) 3283–3289; doi: [org/10.1021/cg400683u](https://doi.org/10.1021/cg400683u)
- [253] K. Alhameedi, A. Karton, D. Jayatilaka, S. P. Thomas, *IUCrJ* 5 (2018) 635–646; doi: [org/10.1107/S2052252518010758](https://doi.org/10.1107/S2052252518010758)
- [254] X. Guo, X. An, Q. Li, Q. J. *Phys. Chem. A* 119 (2015) 3518–3527; doi: [org/10.1021/acs.jpca.5b00783](https://doi.org/10.1021/acs.jpca.5b00783)
- [255] P. Politzer, J. S. Murray, T. Clark, G. Resnati, *Phys. Chem. Chem. Phys.* 19 (2017) 32166–32178; doi: [org/10.1039/C7CP06793C](https://doi.org/10.1039/C7CP06793C)
- [256] R. Wysokiński, M. Michalczyk, W. Zierkiewicz, S. Scheiner, *Phys. Chem. Chem. Phys.* 21 (2019) 10336–10346; doi: [10.1039/C9CP01759C](https://doi.org/10.1039/C9CP01759C)
- [257] Z. Jin, X. Du, Y. Xu, Y. Deng, M. Liu, Y. Zhao, B. Zhang, X. Li, L. Zhang, C. Peng, Y. Duan, J. Yu, L. Wang, K. Yang, F. Liu, R. Jiang, X. Yang, T. You, X. Liu, X. Yang, F. Bai, H. Liu, X. Liu, L.W. Guddat, W. Xu, G. Xiao, C. Qin, Z. Shi, H. Jiang, Z. Rao, H. Yang, *Nature* 582 (2020) 289–293; doi: [org/10.1038/s41586-020-2223-y](https://doi.org/10.1038/s41586-020-2223-y)
- [258] H. Sies, M.J. Parnham, *Free Radic. Biol. Med.* 156 (2020) 107–112; doi: [org/10.1016/j.freeradbiomed.2020.06.032](https://doi.org/10.1016/j.freeradbiomed.2020.06.032)



- [259] J. Struppe, Y. Zhang, S. Rozovsky, *J. Phys. Chemistry B* 119 (2015) 3643–3650; doi: 10.1021/jp510857s
- [260] C.A. Bayse, S. Antony, *Main Group Met. Chem.* 6 (2007) 185–200, doi: 10.1080/10241220801994700
- [261] R. Kheirabadi, M. Izadyar, *M. J. Phys. Chem. A* 120 (2016) 10108–10115; doi: 10.1021/acs.jpca.6b11437